

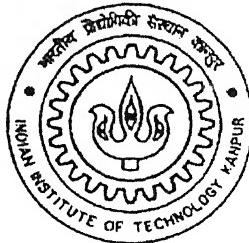
Prediction of Vapor-Liquid Equilibrium Data: A comparison of Cubic and Quartic Equations of State

*A Thesis submitted
in partial fulfilment of the requirements
for the degree of*

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by

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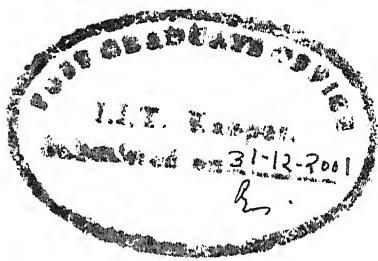
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CERTIFICATE

This is to certify that the work contained in the thesis entitled "**Prediction of Vapor-Liquid Equilibrium Data: A Comparison of Cubic and Quartic Equations of State**" has been carried out by **V. Vamsi Krishna** under my supervision and that this work has not been submitted elsewhere for a degree.



26/12/01
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Abstract

The prediction of phase equilibrium behavior of complex mixtures over broad ranges of temperature and pressure is an important problem in chemical process design. Although cubic Equations Of State (EOS) are widely used in the prediction of Vapor-Liquid Equilibrium (VLE) data, they do not model the repulsive forces correctly and also they do not have the appropriate theoretical background. This work employs generalized Quartic EOS based on the Perturbed-hard-chain-theory, which is the basis of several successful EOS. The Quartic EOS incorporates dipole moment instead of critical pressure, which is used in cubic EOS. This work aims at prediction and comparison of VLE data for thirty-four different systems of seven different classes using four different models. Model-1 uses the Peng-Robinson (PR) EOS with classical van der Waals one fluid mixing rule with single binary interaction parameter. Model-2 employs the PR EOS with composition dependent mixing rules of the Margules type with two binary interaction parameters, whereas Model-3 and Model-4 relies on Quartic EOS with the van der Waals one fluid mixing rule and composition dependent mixing rules, respectively. The results indicate that the Model-2 is the most suitable for the prediction of VLE data. It is also revealed that the mixing rules with two binary interaction parameters predict the VLE data much better than vdW single binary interaction parameter mixing rule. This is true for both PR and Quartic EOS.

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Nomenclature

Alphabets

A_{ij}	Three suffix Margules parameter
A_{ij}	Van Laar parameter
a	Parameter in Equation of state, Activity
a_{mn}	Group interaction parameter
a_{ij}	Cross term of energy parameter a in mixing rules
B, B'	Second Virial coefficient
b_{ij}	Cross term of volume parameter b in mixing rules
C, C'	Third Virial coefficient
c	Parameter of the quartic equation of state
d	Parameter of PR EOS
e	Parameter of the quartic equation of state
f	Fugacity
\hat{f}_i	Fugacity of component i in the mixture
G_{ij}	NRTL parameter
g	Molar Gibbs free energy
g^E	Molar excess Gibbs free energy
\tilde{g}^E	Partial Molar Gibbs free energy
g_{ij}	Energy parameter in NRTL equation
k_{ij}, k_{ji}	Binary interaction parameters
K_I	Equilibrium constant
l_{ij}	Binary interaction parameter
m_{ij}	Binary interaction parameter
n	Number of moles
N	Number of data points
P	Pressure
Q_k	Group area parameter
q_1, q_2	Measure of volume of component

q	Surface area parameter in UNIQUAC
R	Universal gas constant
R_k	Group volume parameter
r_i	Volume parameter of component i in UNIQUAC
T	Temperature
u_{ij}	Average interaction energy for the interaction of component i with the component j
u_{mn}	Measure of interaction energy between groups m and n
V	Volume
ν	Molar volume
$\bar{\nu}_i$	Partial molar volume of component I
X_i	Quartic equation of state regressed coefficient
x_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in vapor phase
Z	Compressibility factor
z	Co-ordination number
z_1, z_2	Volume fractions

Greek letters

α	Temperature dependence of parameter a
α_{ij}	Non-randomness parameter in NRTL equation
β	Hard core volume
Γ_i	Integration constant
Γ_k	Group residual activity coefficient
Γ_k^i	Residual activity coefficient of group k in a reference solution containing only molecule of type i
γ	Activity coefficient
τ_{ij}	NRTL parameter, UNIQUAC parameter
θ_i	Area fraction of component i

Λ	Thermal deBroglie wavelength
Λ_{ij}	Wilson parameter
λ_{ij}	Energy parameter in Wilson equation
μ	Chemical potential, dipole moment of the polar fluid in debye units
ν_k^i	Number of groups of type in a molecule of component I
κ	Function of acentric factor
ϕ	Fugacity coefficient
ϕ_i	Segment fraction of component i
$\hat{\phi}_i$	Fugacity coefficient of component i in mixture
ξ	Temperature dependence of parameter c in Quartic EOS
ψ_{mn}	UNIFAC parameter
ω	Acentric factor
Δ	Average deviation

Superscripts

E	Excess
l	Liquid phase
o	Reference state
s	Saturated
v	Vapor phase
$*$	Reduced variable

Subscripts

c	Critical property
i,j	Molecular species
m	mixtures
r	Reduced property
t	Total basis

CHAPTER 1

INTRODUCTION

The estimation of phase equilibrium behavior of complex mixtures over broad ranges of temperature and pressure is an important problem in chemical process design as most of the chemical industrial processes deal with operations such as, extraction, adsorption, distillation, leaching, and absorption, which involve phase contacting. In particular distillation is the most important separation and purification process used in chemical industry, where vapor and liquid phases co-exist. This requires the process designer to have a reliable Vapor-Liquid Equilibria (VLE) data, for design of distillation columns. Though for a large number of binary and for a few multi-component systems the experimental VLE data can be found in literature, the experimental data is not available at all desired conditions. This necessitates the designer either to experimentally determine or estimate the required VLE data. But if the process of interest is to be performed over a wide range of pressures and temperatures, the number of experimental points required becomes large. Hence the available experimental data can be used to develop a model, which in turn can be used to predict the data at the required operating conditions.

The available models for the prediction of VLE data can be broadly classified as activity coefficient models and Equation Of State (EOS) models. In activity coefficient model the liquid phase non-ideality is described in terms of an activity coefficient (γ_i) for component i of the system. The vapor phase non-ideality is expressed in terms of fugacity coefficient (ϕ_i) for component i of the system. The fugacity coefficient can be obtained by making use of an appropriate equation of state. Some of the models that belong to this method are Margules, van Laar, UNIFAC etc., (Rao Y. V. C. 1997). In EOS approach both the liquid and vapor phase non-idealities are explained by the fugacity coefficient where, it is indicated by (ϕ_i^l) for the liquid phase and (ϕ_i^v) for the vapor phase. Some of the equations of state such as Peng-Robinson (PR), Soave-Redlich-Kwong (SRK), Peng-Robinson-Stryjek-Vera (PRSV), Benedict-Webb-Rubin (WBR) are used in this method (Mark et al. 1991).

The activity coefficient models give satisfactory results at low to moderate pressures. However, their applications at critical and supercritical pressures yield inaccurate VLE data. EOS approach is a powerful tool for addressing this problem. The major advantage of the EOS approach is its applicability over a wide range of temperatures and pressures including critical and supercritical, where the activity coefficient models fail. In process simulation calculations, the equations of state are widely used due to their algebraic simplicity and their accuracy.

There are two requirements for the equations of state to be successful. (1) The EOS must predict the saturation pressure of pure substances accurately. (2) The mixing rules must be available which correctly extend these equations to multicomponent mixtures. Different equations of state predict the thermodynamic properties with different degrees of accuracy and they require different types of data for proper evaluation. Hence, a reliable EOS for practical applications must be physically sound, reasonably simple and present no convergence problems.

There has been significant improvement in the accuracy of cubic equations of state for the prediction of pure component properties in the last two decades (Sandler et al., 1994). Cubic equations of state, which are in wide use, model the repulsive forces incorrectly resulting in inaccuracies in representing the thermodynamic properties, especially in the supercritical fluid and condensed phase regions. Van der Waals proposed the first cubic equation of state in 1873. The well-documented van der Waals equation is the most influential EOS that incorporated both the repulsion and attraction of intermolecular forces in the expression. Numerous EOS have since been proposed within the framework of this concept (Anderko (1990)). Redlich and Kwong (1949) modified the attractive term of the expression of the van der Waals EOS, but retained its repulsive term, to satisfy the boundary conditions in the low and high-density limits. The Redlich-Kwong (RK) EOS is among the most fruitful of the van der Waals family for routine engineering calculations. Various modifications of the RK equation to improve its accuracy have also been suggested. These are represented by the Soave (1972) and the Peng and Robinson (1976) equations.

The modifications are mostly empirical and arbitrary, although in some instances physical constraints were proposed. All these equations of van der Waals family are explicit in pressure and third order in volume for which the equation can be solved analytically. The van der Waals EOS and its modifications account for the repulsive contribution to pressure with an excluded volume term $RT/(V-b)$ that is conceptually incorrect at high densities. This term overestimates the repulsive pressure in comparison with the results from molecular simulations. The success of EOS of the van der Waal's family is probably due to the mutual cancellation of errors in the repulsive and attractive terms. In order to overcome some of these deficiencies and to develop a theoretically based EOS which is capable of representing both the vapor and the liquid phases, Beret and Prausnitz (1975) proposed the perturbed-hard-chain-theory. This theory is the basis of several successful EOS. A feature of the perturbed-hard-chain-theory is the factorization of partition function into internal and external contributions. The density dependence of all external degrees of freedom is assumed to be same as those of the translational degrees of freedom, which is represented by Carnahan and Starling (1969) equation. Kubic (1986) proposed the Quartic hard chain equation of state. Shah et al., (1994) proposed the generalized Quartic EOS for pure non-polar fluids. Later Shah et al., (1996) proposed the Extended Generalized Quartic equation of state for pure polar fluids. The Quartic EOS retains the desirable features of the popular cubic EOS with improved accuracy.

The extension of equations of state to describe phase behavior for a broad range of multicomponent mixtures had been more difficult due to limited applicability of the van der Waals (vdW) one-fluid mixing rules that are commonly used for relatively simple mixtures. The vdW mixing rules are incapable of representing the highly non-ideal mixture behavior of polar or associating fluids. Consequently, much effort in recent years has been devoted toward developing alternative mixing rules to extend the cubic equations of state to complex mixtures [Orbey and sandler (1996); Heidemann (1996)]. With the advent of multiparameter mixing rules, equations of state are now being used for the phase equilibrium calculations of complex mixtures that were traditionally described with activity coefficient models.

The present work deals with a comparison of Quartic EOS with Peng-Robinson (PR) EOS for the estimation of VLE data using two different mixing rules. The generalized quartic equation of state has been used to predict the VLE data. The quartic EOS has four roots. The identification of these roots is very easy as, one root is always negative which has no physical significance. Hence, the rules used to identify the roots of cubic EOS could be used with quartic EOS also. This makes the prediction of volumes at different temperatures and pressures possible, by solving the corresponding equation of state in terms of the compressibility factor (Z) or volume (v).

VLE calculations are done using Quartic EOS and PR EOS, for binary mixtures of hydrocarbons, alcohols, and refrigerants. Van der Waals one fluid mixing rules and composition dependent mixing rules [Huron and Vidal (1979); Stryjek and Vera (1986)] are used with each EOS for the VLE calculations. The results are then compared with the available experimental data. The Quartic EOS with composition dependent mixing rules predicts accurate VLE data for alcohol-alcohol mixtures. For alcohol-hydrocarbon mixtures the PR EOS with composition dependent mixing rules predicts accurate VLE data except for the mixtures that contain butanol as one component for which the Quartic EOS with composition dependent mixing rules predicts accurate VLE data. For hydrocarbon-hydrocarbon mixtures the PR EOS with composition dependent mixing rules is as good as the Quartic EOS with composition dependent mixing rules. For refrigerant mixtures, in most cases, the PR EOS with composition dependent mixing rules predicts extremely accurate VLE data. However, the Quartic EOS with composition dependent mixing rules is also equally good.

CHAPTER 2

PHASE EQUILIBRIUM AND MIXING RULES

2.1 Equilibrium Criterion

For a closed system containing vapor and liquid phases, with each phase consisting of c components, in a state of equilibrium at constant temperature (T) and pressure (P), the criterion for equilibrium is given by (Smith et al. 1996),

$$\mu_i^l = \mu_i^v \quad (i = 1, 2, \dots, c) \quad (2.1)$$

where, μ_i^l and μ_i^v are chemical potentials of component i in liquid and vapor phases, respectively. The chemical potential μ_i , is given

$$\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i \quad (2.2)$$

where $\Gamma_i(T)$, an integration constant, is a function of temperature only and \hat{f}_i is the fugacity of component i in the mixture. Using Eq. (2.2) in Eq. (2.1), the general criterion for vapor-liquid equilibrium reduces to

$$\hat{f}_i^l = \hat{f}_i^v \quad (i = 1, 2, \dots, c) \quad (2.3)$$

The Eq. (2.3) can be rewritten as (Rao Y. V. C. 1997),

$$\gamma_i x_i f_i^0 = \hat{\phi}_i^v y_i P \quad (i = 1, 2, \dots, c) \quad (2.4)$$

where γ_i = activity coefficient of component i in the solution.

x_i, y_i = mole fractions of component i in liquid and vapor phases, respectively.

f_i^0 = fugacity of component i in the standard state.

$\hat{\phi}_i^v$ = fugacity coefficient of component i in the vapor phase.

P = Pressure at which the system is held.

The standard state fugacity (f_i^0) is the fugacity of component i at the mixture temperature and at some arbitrarily chosen pressure and composition. The standard state for component i , is chosen as the liquid phase of the pure component i at the system temperature and pressure. With this choice of the standard state, f_i^0 is given by,

$$f_i^0 = P_i^s \phi_i^s \exp \left\{ \frac{v_i^l (P - P_i^s)}{RT} \right\} \quad (2.5)$$

where, ϕ_i^s is the fugacity coefficient of component i at saturation pressure P_i^s for the same component i at temperature T . v_i^l is the molar volume of liquid for component i . Substitution of Eq. (2.5) in Eq. (2.4) results in the *basic equation for vapor-liquid equilibrium*, which is given by

$$\gamma_i x_i P_i^s = \frac{\hat{\phi}_i^v}{\phi_i^s} y_i P \exp \left\{ \frac{v_i^l (P - P_i^s)}{RT} \right\} \quad (i = 1, 2, \dots, c) \quad (2.6)$$

At low pressures, the vapor phase can be assumed to behave like an ideal gas. Hence $\hat{\phi}_i^v = 1$ and $\phi_i^s = 1$. Moreover, the Pointing correction factor (exponential term in Eq. (2.6)) is approximately equal to unity. At moderate pressures $\hat{\phi}_i^v$ and ϕ_i^s are approximately equal and hence it is reasonable to assume that $(\hat{\phi}_i^v / \phi_i^s) = 1$. Thus at low to moderate pressures Eq. (2.6) reduces to

$$\gamma_i x_i P_i^s = y_i P \quad (1, 2, \dots, c) \quad (2.7)$$

$$\text{or} \quad \gamma_i = \frac{y_i P}{x_i P_i^s} \quad (1, 2, \dots, c) \quad (2.8)$$

However, at high pressures these assumptions are not valid. Eq (2.3) can also be written as

$$\hat{\phi}_i^l x_i P = \hat{\phi}_i^v y_i P \quad (\text{since } \hat{\phi}_i = (\hat{f}_i / y_i P))$$

$$\text{or} \quad \hat{\phi}_i^l x_i = \hat{\phi}_i^v y_i \quad (1, 2, \dots, c) \quad (2.9)$$

$$\text{or} \quad K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^l}{\hat{\phi}_i^v} \quad (1, 2, \dots, c) \quad (2.10)$$

where K_i is the K factor or equilibrium constant for component i .

The methods available for the prediction of VLE data can be broadly classified as

1. Activity coefficient Approach
2. Equation of State (EOS) Approach

The main difference between the two methods lies in the reference state. For the EOS method, the reference state is the ideal gas condition and the fugacity coefficient is a measure of the deviation from this state for both the vapor and liquid phases. For activity coefficient methods, the reference state for the liquid is the pure liquid at the same temperature and pressure of the mixture. The choice of the thermodynamic model to be used depends on

- Nature of the components
- The pressure and temperature conditions

NATURE OF THE COMPONENTS

The nature of the component decides the extent of non-ideality. Non-ideality is due to the interaction between the molecules, which depends on intermolecular forces. This interaction is more evident in the liquid phase where the molecules are packed closer. The choice between the EOS method and Activity coefficient method can be made based on the polar nature of the components.

Hydrocarbons like ethane, propane, pentane are non-polar and can be represented adequately by EOS methods. Mixtures of polar compounds may be represented using Activity coefficient methods. Mixtures of polar and non-polar compounds can give rise to two immiscible liquid phases and hence a model that is capable of predicting a phase split must be considered. This would be an Activity Coefficient method like NRTL or UNIQUAC. Wilson or Van Laar models are incapable of predicting splitting of the liquid phase.

TEMPERATURE AND PRESSURE

At high pressures and at temperatures above critical, the activity coefficient models fail. EOS models are valid over a wide range of temperature and pressure. Since consistency is inherent in the EOS approach, these are applicable even at the critical conditions.

2.2 Activity Coefficient Approach

The basis of activity coefficient approach is the activity, which is defined as

$$a_i = \frac{f_i(T, P, x_i)}{f_i^0(T, P^0, x_i^0)} \quad (2.11)$$

Here a_i is the activity of component i and f_i^0 is the standard state fugacity (at some arbitrarily defined pressure P^0 and some arbitrarily defined composition x_i^0). The activity coefficient γ_i is defined as

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i}{x_i f_i^0} \quad (2.12)$$

The partial molar Gibbs free energy is given by

$$\mu_i - \mu_i^0 = \tilde{g}_{i,real} - \tilde{g}_{i,ideal} = \tilde{g}_i^E = RT \ln \frac{f_i^l}{f_{i,ideal}} \quad (2.13)$$

From Raoult's law one can obtain

$$f_{i,ideal} = x_i f_i^0 \quad (2.14)$$

$$\tilde{g}_i^E = RT \ln \frac{\gamma_i x_i f_i^0}{x_i f_i^0} = RT \ln \gamma_i \quad (2.15)$$

Using the definition of partial molar excess Gibbs free energy, one can obtain

$$\ln \gamma_i = \frac{1}{RT} \left[\frac{\partial (ng^E)}{\partial n_i} \right]_{T,P,n_j} \quad (2.16)$$

where, g^E = molar excess Gibbs energy. The relation between g^E and the activity coefficients can also be expressed as

$$g^E = \sum_{i=1}^c x_i \tilde{g}_i^E = RT \sum_{i=1}^c x_i \ln \gamma_i \quad (2.17)$$

The Gibbs-Duhem relation for a binary mixture is given by

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} \quad (2.18)$$

Assume that g^E can be expressed as a function of temperature, pressure and composition. That is,

$$g^E = f(T, P, x_i) \quad (2.19)$$

The Activity coefficient can then be derived from Eq. (2.16) and substituted into the following equilibrium constraint.

$$y_i P \phi_i^v = \gamma_i(T, P, x_i) x_i f_i^0 \quad (2.20)$$

The system of equations defined by Eq. (2.20) can be solved for the equilibrium temperature, pressure, and concentration. Therefore, the basis of activity coefficient approach is to find an accurate form of Eq. (2.19).

The commonly used Activity coefficient models are

- Margules Equation
- Van Laar Equation
- Wilson Equation
- NRTL Equation
- UNIQUAC Equation
- UNIFAC Equation

2.2.1 Margules Equation

The Margules equations, can be deduced from the expressions for excess Gibbs free energy given by Wohl's expansion (Mark et al. 1991)

$$\frac{g^E}{RT(x_1 q_1 + x_2 q_2)} = 2a_{12}z_1 z_2 + 3a_{112}z_1^2 z_2 + 3a_{122}z_1 z_2^2 + \dots \quad (2.21)$$

where

$$z_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2} = \text{the volume fraction of component } i \quad (2.22)$$

q_i = measure of volume of the component i . a_{12} , a_{112} , a_{122} are empirical constants which signify two body, three body,.... interactions.

Margules assumed the size of molecules to be equal ($q_1 = q_2$). After some rearrangements Eq. (2.21) reduces to the Margules three suffix equation given by

$$\frac{g^E}{RT} = (A_{12} x_1 + A_{21} x_2) x_1 x_2 \quad (2.23)$$

where A_{12} and A_{21} are adjustable parameters.

The activity coefficients γ_1 and γ_2 are given by

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \quad (2.24)$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1^2 \quad (2.25)$$

The Margules three suffix equations are used for symmetrical systems ($q_1 = q_2$) i.e. systems where all the components have almost equal size.

2.2.2 Van Laar Equation

Margules equation assumes equal size for molecules, which is not true. If the size difference of the molecules ($q_1 \neq q_2$) is incorporated into Wohl's expansion, (Mark et al. 1991) it gives

$$\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1 + x_2q_2} \quad (2.26)$$

Simplifying Eq. (2.26) leads to van Laar equations, which are given by

$$\frac{g^E}{RT} = \frac{A_{12}A_{21}x_1x_2}{x_1A_{12} + x_2A_{21}} \quad (2.27)$$

$$\ln \gamma_1 = A_{12} \left[\frac{A_{21}x_2}{x_1A_{12} + x_2A_{21}} \right]^2 \quad (2.28)$$

$$\ln \gamma_2 = A_{21} \left[\frac{A_{12}x_1}{x_1A_{12} + x_2A_{21}} \right]^2 \quad (2.29)$$

where A_{12} and A_{21} are adjustable parameters.

2.2.3 Wilson Equation

For Mixtures in which the components differ from each other in molecular size and interaction between the unlike and like molecules are different, Wilson (1964) proposed the following expression for the excess Gibbs free energy of a binary solution.

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \quad (2.30)$$

where Λ_{12} and Λ_{21} are two adjustable parameters, which are related to pure component molar volumes and characteristic energy differences.

Λ_{12} and Λ_{21} are given by

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\frac{\lambda_{12} - \lambda_{21}}{RT}\right] \quad (2.31)$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left[-\frac{\lambda_{12} - \lambda_{21}}{RT}\right] \quad (2.32)$$

v_i =molar volume of pure component i .

λ_{ij} =energy of interaction between molecules of component i and j .

The activity coefficients can be derived from Equation (2.30) and are given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (2.33)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (2.34)$$

2.2.4 Non-Random Two Liquid (NRTL) Equation

The Non-Random Two Liquid (NRTL) equation proposed by Renon and prausnitz (1968) is applicable to partially miscible as well as completely miscible systems.

The NRTL equation for excess Gibbs free energy is given by

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + G_{12} x_2} + \frac{\tau_{12} G_{12}}{x_2 + G_{21} x_1} \right] \quad (2.35)$$

where

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \quad (2.36)$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad (2.37)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad (2.38)$$

$$G_{21} = \exp(-\alpha_{21} \tau_{21}) \quad (2.39)$$

g_{ij} =energy of interaction between molecules of component i and j .

The parameter α_{ij} is introduced to take into account the non-randomness of the mixture. If $\alpha_{ij}=0$, the mixture is completely random and Equation (2.35) reduces to Margules equation. The activity coefficients can be derived from Equation (2.35) and are given by

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + G_{21}x_2} \right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + G_{21}x_1)^2} \right] \quad (2.40)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + G_{12}x_1} \right)^2 + \frac{\tau_{21}G_{12}}{(x_1 + G_{12}x_2)^2} \right] \quad (2.41)$$

The NRTL equation does not provide any additional advantage over Margules and Van Laar equations for moderately non-ideal solutions, but it represents the excess Gibbs free energy of strong non-ideal and partially miscible systems quite satisfactorily.

2.2.5 UNIversal QUAsi Chemical (UNIQUAC) Equation

To express the excess Gibbs free energy of a binary mixture, Abrams and Prausnitz (1975) developed the UNIversal QUAsi Chemical (UNIQUAC) model. The UNIQUAC equation for (g^E/RT) contains two parts - a combinatorial part and a residual part. The combinatorial part takes into account the composition, size and shape of the constituent molecules and contains pure component properties only. The residual part takes into account the intermolecular forces and contains two adjustable parameters. The UNIQUAC equation is given by

$$\frac{g^E}{RT} = \frac{g^E}{RT}(\text{combinatorial}) + \frac{g^E}{RT}(\text{residual}) \quad (2.42)$$

where

$$\frac{g^E}{RT}(\text{combinatorial}) = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{z}{2} \left(q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2} \right) \quad (2.43)$$

$$\frac{g^E}{RT}(\text{residual}) = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{12}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{21}) \quad (2.44)$$

$$\phi_i = \text{segment fraction of component } i = \left(x_i r_i / \sum_j x_j r_j \right) \quad (2.45)$$

$$\theta_i = \text{area fraction of component } i = \left(x_i q_i / \sum_j x_j q_j \right) \quad (2.46)$$

r_i = volume parameter of component i

q_i = surface area parameter of component I

$$\tau_{ij} = \exp\left\{-\frac{(u_{ij} - u_{ii})}{RT}\right\} = \exp\left(-\frac{a_{ij}}{T}\right) = \text{adjustable parameter} \quad (2.47)$$

u_{ij} =average interaction energy for the interaction of molecules of component i with the molecules of component j ; and

z = coordination number which is usually taken as 10.

From Eqs. 2.42-2.47 one can obtain the activity coefficients as

$$\ln \gamma_i = \ln \gamma_i^c (\text{combinatorial}) + \ln \gamma_i^R (\text{residual}) \quad (2.48)$$

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_i l_i \quad (2.49)$$

$$\ln \gamma_i^R = q_i \left[1 - \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ji}}{\left(\sum_k \theta_k \tau_{ki} \right)} \right] \quad (2.50)$$

where $l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1)$ (2.51)

The structural parameters r_i and q_i are calculated as the sum of product of the group volume and parameters R_k and Q_k .

$$r_i = \sum_k v_k^{(i)} R_k \quad (2.52)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (2.53)$$

where $v_k^{(i)}$ is the number of groups of type k in a molecule of component i . The UNIQUAC equation is applicable to a wide variety of liquid solutions commonly encountered by chemical engineers.

2.2.6 UNIquac Functional group Activity Coefficients (UNIFAC) Method (group contribution method)

To correlate and to predict the thermodynamic properties of a solution it was convenient to consider the component molecules as a collection of functional groups. The functional groups are structural units such as $-\text{CH}_3$, $-\text{OH}$ and others which when added form the constituent molecules. In the group contribution methods, a solution of components is treated as a solution of groups. The activity coefficients of the

components are then determined by the properties of the functional groups rather than by those of the molecules. The basic idea behind this approach is that there are several thousands of chemical compounds that are of interest to a chemical engineer but the number of functional groups, which constitute these compounds, is very small. The activity coefficients in a large number of solutions can be calculated from the parameters characteristic of the functional groups.

In the UNIFAC method the activity coefficients consist of two parts, a combinatorial part ($\ln\gamma_i^c$) and a residual part ($\ln\gamma_i^R$). The combinatorial part of activity coefficient $\ln\gamma_i^c$ given by Eq. (2.46) of UNIQUAC method is directly used. To evaluate $\ln\gamma_i^c$ only pure component data is required. One identifies the functional subgroups present in each molecule and estimates the parameters r_i and q_i as the sum of the group volume and area parameter R_k and Q_k by using the Eqs. (2.52) and (2.53).

The residual part of the activity coefficient $\ln\gamma_i^R$ is given by

$$\ln\gamma_i^R = \sum_k v_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (2.54)$$

where

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right] \quad (2.55)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} = \text{surface area fraction of group } m \quad (2.56)$$

$$\psi_{mn} = \exp \left(- \frac{u_{mn} - u_{nn}}{RT} \right) = \exp \left(- \frac{a_{mn}}{T} \right) \quad (2.57)$$

x_m = mole fraction of group m in the mixture

a_{mn} = group interaction parameter (in K). $a_{mn} \neq a_{nm}$

u_{mn} = measure of interaction energy between groups m and n

Γ_k = group residual activity coefficient; and

$\Gamma_k^{(i)}$ = residual activity coefficient of group k in a reference solution containing only molecules of type i .

2.2.7 Advantages and Disadvantages of Activity Coefficient Approach

A simplifying assumption that is made in the development of activity coefficient models is that g^E is independent of pressure. In view of this assumption, the activity coefficient approach can be applied to systems at low to moderate pressures, far removed from the critical. For processes that operate near or above the critical, the activity coefficient approach cannot be used, which is by far the greatest deficiency of this approach.

The activity coefficient approach should be used to treat low pressure VLE data. The activity coefficient approach can be successfully applied to various types of systems: mixtures of alcohols with hydrocarbons, non-polar hydrocarbon mixtures and mixtures of alcohols with other polar compounds. In addition, systems with limited miscibility have been successfully treated with activity coefficient approach.

2.3 Equation of State Approach

In the equation of state method, a single equation of state is used to represent all fluid phases. From the thermodynamic point of view, this is a potentially more powerful approach as it provides a uniform representation of the thermodynamic properties in the two-phase and one-phase regions with a single equation. It is not only applicable to wide pressure and temperature ranges including critical and supercritical conditions but also makes it possible to calculate phase equilibria data. According to the review by Kolasinska (1986), depending on the form of equation of state variables, the equation of state may be classified into the following types.

1. Non analytical
2. Analytical
 - a) inspired on a Virial expansion
 - b) inspired on the two-term van der Waals form

Equations of state inspired on the two-term van der Waals form were found to be most attractive due to their simplicity, low computational costs and reliability. Non-analytical types of equations are not presented here. A brief account of the analytical type of EOS is presented below. The simplest EOS is the ideal gas equation ($PV = nRT$) which considers that there are no interactions between molecules.

2.3.1 Virial EOS

In real gases molecular interactions always exist. This is explained by the Virial EOS where PV is expressed as a power series in P (Smith et al. 1996).

$$PV = a + bP + cP^2 + \dots \quad (2.58)$$

$$PV = a(1 + B'P + C'P^2 + \dots) \quad (2.59)$$

Where, a , B' , C' are constants at a given temperature for a given species. When $a = RT$, Eq. (2.59) reduces to

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + \dots \quad (2.60)$$

or alternatively

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \quad (2.61)$$

Where, Eq. (2.60) or (2.61) is called Virial equation of state, Z is the compressibility factor and B , C , D etc., (or B' , C' , D' etc.,) are called virial coefficients. The virial EOS is not used in phase-equilibrium studies as it can describe only vapor phase behavior.

Equations inspired on the two term van der Waals form

In general equations based on the van der Waals model are in a form where total pressure is the sum of an attractive and a repulsive pressure term (Kolasinska 1986).

$$P = P_{(repulsive)} + P_{(attractive)} \quad (2.62)$$

This form is proposed to take into account the attractive and repulsive forces existing in the real fluids. Imagine two molecules as hard spheres. When the molecules are at a large distance from each other they experience small or no attractive forces. As the distance between the molecules is decreased, the attractive forces get larger, until the

hard spheres come close to each other. Once the molecules come close to each other, repulsive forces start dominating until the molecules can get close no further. This volume is unavailable for the molecular motion. Van der Waals took the unavailable volume into account by introducing a parameter b called the ‘excluded volume’.

2.3.2 van der Waals Equation of State (vdW)

When expressed in the form of Eq. (2.62) the van der Waals equation is given by,

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (2.63)$$

$$P_{\text{repulsive}} = \frac{RT}{v-b} \quad (2.64)$$

$$P_{\text{attractive}} = -\frac{a}{v^2} \quad (2.65)$$

The values of a and b can be found by regressing vapor pressure data and choosing a and b that best fit that data or alternatively critical point conditions are used. At the critical point, the first and second derivatives of pressure with respect to volume at constant temperature are zero. When these conditions are applied to Eq. (2.63), the values of a and b turn out to be

$$a = \frac{27R^2T_c^2}{64P_c} \quad (2.66)$$

$$b = \frac{RT_c}{8P_c} \quad (2.67)$$

2.3.3 Redlich-Kwong Equation of State

An important modification of the van der Waals equation of state was made by Redlich and Kowng (1949), who introduced a temperature dependence and slightly different volume dependence in the attractive term. The Redlich-Kwong Equation of State (RK EOS) is given by

$$P = \frac{RT}{v-b} - \frac{a}{T^{2.5}v(v+b)} \quad (2.68)$$

where

$$a = 0.42748 \frac{R^2 T_c^2}{P_c} \quad (2.69)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (2.70)$$

These modifications improved the accuracy of the equation. As before, the values of a and b can be found by fitting vapor pressure data or by using the conditions at the critical point. The RK EOS has limited accuracy, and is generally successful only for nearly ideal systems. To overcome these deficiencies, many modifications have been proposed over the years. Two of these modifications have achieved wide acceptance – the Soave and the Peng-Robinson equations of state.

2.3.4 Soave-Redlich-Kowng Equation of State

Soave (1972) proposed a modification to the RK Equation incorporating the temperature dependency to the EOS parameter a as

$$a(T) = a_c \alpha(T) \quad (2.71)$$

where

$$\alpha(T) = \left\{ 1 + (0.48 + 1.57\omega - 0.176\omega^2)(1 - \sqrt{T_r}) \right\} \quad (2.72)$$

and ω is the Pitzer (1995) acentric factor defined as

$$\omega = \left[-\log \frac{(P)_{T_r=0.7}}{P_c} - 1.0 \right] \quad (2.73)$$

$$T_r = (T/T_c) = \text{reduced temperature} \quad (2.74)$$

Thus, the EOS proposed by Soave is of the form

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (2.75)$$

When calculating fugacity coefficients, it is convenient to write the equation in terms of the compressibility factor Z . In this form the Soave equation of state is

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (2.76)$$

where

$$A = \frac{aP}{R^2 T^2} \quad (2.77)$$

$$B = \frac{bP}{RT} \quad (2.78)$$

$$Z = \frac{Pv}{RT} \quad (2.79)$$

The van der Waals one fluid mixing rules are used for calculating a and b of the mixture. Thus the fugacity coefficient of component i in a mixture is given by

$$\ln \phi_i = \frac{b}{b_i} (Z - 1) - \ln(Z - B) + \frac{a}{bRT} \left[\frac{b_i}{b} - 2\sqrt{\frac{a_i}{a}} \right] \ln \left[\frac{Z + B}{Z} \right] \quad (2.80)$$

2.3.5 Peng-Robinson Equation of State

In 1976, Peng and Robinson introduced another equation of state, which extended some of the ideas presented by Soave. The repulsive part of the van der Waals model remained the same, but just as Soave had done, the temperature dependence of the attractive term was incorporated into the a term. The denominator of the attractive term was also changed to a slightly more complicated expression of volume and the size parameter. The Peng-Robinson Equation of State is given by

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (2.81)$$

The values of the parameters were obtained by following the method as in SRK EOS,

$$b = 0.07780 \frac{RT_c}{P_c} \quad (2.82)$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (2.83)$$

$$a(T) = a(T_c)\alpha \quad (2.84)$$

$$\alpha^{\frac{1}{2}} = 1 + \kappa(1 - T_r^{\frac{1}{2}}) \quad (2.85)$$

$$\text{where reduced temperature } T_r = T/T_c \quad (2.86)$$

$$\kappa = f(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (2.87)$$

2.3.6 Peng-Robinson-Stryjek-Vera EOS

In order to make the Peng-Robinson EOS more widely applicable Stryjek and Vera (1986a) modified the temperature and acentric factor dependence of the PR EOS. They also extended it to strongly non-ideal mixtures (Stryjek et al., 1986b). They introduced a pure component parameter into the expression for κ which is slightly modified. The PRSV EOS is given by,

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (2.88)$$

and the parameters a and b are given by

$$b = 0.07780 \frac{RT_c}{P_c} \quad (2.89)$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (2.90)$$

$$a(T) = a(T_c)\alpha \quad (2.91)$$

$$\alpha^{\frac{1}{2}} = 1 + \kappa(1 - T_r^{\frac{1}{2}}) \quad (2.92)$$

$$\text{where reduced temperature} \quad T_r = T/T_c \quad (2.93)$$

In the PRSV equation κ term takes the form

$$\kappa = \kappa_0 + \kappa_1(1 + T_r^{0.5})(0.7 - T_r) \quad (2.94)$$

where κ_1 is the pure component parameter introduced by Stryjek and Vera and κ_0 is given by

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (2.95)$$

2.3.7 Quartic Equation Of State

Kubic (1986) proposed Quartic hard chain EOS and Soave (1990) proposed a new Quartic van der Waals type EOS. Shah et al., (1994) introduced the generalized Quartic EOS for pure non-polar compounds and extended the same for polar compounds (Shah et al., 1996).

The generalized Quartic EOS is given by,

$$P = \frac{RT}{(\nu - k_0\beta)} + \frac{\beta k_1 RT}{(\nu - k_0\beta)^2} - \frac{av + k_0\beta c}{\nu(\nu + e)(\nu - k_0\beta)} \quad (2.96)$$

This equation of state is rewritten as quartic in volume as,

$$\nu^4 + q_3\nu^3 + q_2\nu^2 + q_1\nu + q_0 = 0 \quad (2.97)$$

where

$$q_3 = \left(-2k_0\beta + e - \frac{RT}{P} \right) \quad (2.98)$$

$$q_2 = \left[\frac{RT}{P} (\beta(k_0 - k_1) - e) + k_0\beta(k_0\beta - 2e) \right] + \frac{a}{P} \quad (2.99)$$

$$q_1 = e \left[(k_0\beta)^2 + \frac{RT\beta(k_0 - k_1)}{P} \right] + \left[\frac{k_0\beta(c - a)}{P} \right] \quad (2.100)$$

$$q_0 = -\frac{c(k_0\beta)^2}{P} \quad (2.101)$$

The hard sphere volumes of the fluids at the critical temperature were fixed as 0.165 times the critical volume of the fluids. Temperature dependence was incorporated into β , According to Nezbeda and Aim (1984).

$$\beta = \beta_c \left[\exp \left(-0.03125 \ln(T_r) - 0.0054 (\ln(T_r))^2 \right) \right]^3 \quad (2.102)$$

where

$$\beta_c = 0.165V_c$$

$$a = a_c \alpha(T_r) \quad (2.103)$$

where for $T_r \leq 1$

$$\alpha(T_r) = \left[1 + X_2(1 - \sqrt{T_r}) + X_3(1 - \sqrt{T_r})^2 + X_4(1 - \sqrt{T_r})^3 \right]^2 \quad (2.104)$$

where for $T_r > 1$

$$\alpha(T_r) = \left[1 + X_2(1 - \sqrt{T_r}) + X_5(1 - \sqrt{T_r})^2 + X_6(1 - \sqrt{T_r})^3 \right]^2 \quad (2.105)$$

$$c = c_c \xi(T_r) \quad (2.106)$$

$$\xi(T_r) = [1 + X_7(1 - T_r)]^2 \quad (2.107)$$

where a_c and c_c are the values of a and c at the critical temperature of the fluid, and X_2 , X_3 , X_4 , X_5 , X_6 and X_7 are the constants determined by regression. The equation of state is

extended to non-spherical fluids with the introduction of acentric factor ω as the third property to characterize the fluids. The parameters a , c and e , and the constants X_2 through X_7 are made quadratic functions of acentric factor. The parameters a_c and c_c , related to the acentric factor, are defined as

$$a_c = a_r \frac{RT_c}{\rho_c} \quad (2.108)$$

$$c_c = c_r \frac{RT_c}{\rho_c} \quad (2.109)$$

$$e = \frac{e_r}{\rho_c} \quad (2.110)$$

$$a_r = a_{r0} (1 + a_{r1}\omega + a_{r2}\omega^2) \quad (2.111)$$

$$c_r = c_{r0} (1 + c_{r1}\omega + c_{r2}\omega^2) \quad (2.112)$$

$$e_r = e_{r0} (1 + e_{r1}\omega + e_{r2}\omega^2) \quad (2.113)$$

The values of a_{r0} , a_{r1} , a_{r2} , c_{r0} , c_{r1} , c_{r2} , e_{r0} , e_{r1} , e_{r2} are obtained by regression and the constants X_2 to X_7 are made functions of ω as

$$X_i = X_{i1} + X_{i2}\omega \quad (2.114)$$

for $i=2,3,4,5,6,7$

Extension of the Generalized Quartic EOS to Polar Fluids

To apply the Quartic equation of state to polar compounds, the parameters a and c are assumed to be functions of the acentric factor and the dipole moment of the fluid. In order to express the parameters of the quartic equation in the dimensionless form, the reduced dipole moment (μ^*) is defined below

$$\mu^* = \frac{0.3976\mu}{(RT_c V_c)^{0.5}} \quad (2.115)$$

where μ is the dipole moment of the polar fluid in debye units.

For polar fluids, the regressed coefficients X_2 through X_7 are made linear functions of the acentric factor and the quadratic functions of the reduced dipole moment. The regressed

constants a_r and c_r are made quadratic functions of the acentric factor and the reduced dipole moment, and are given by

$$X_I = X_{i1} + X_{i2} + X_{i3}\mu^* + X_{i4}\mu^{*2} \quad (2.116)$$

$$a_r = a_{r0} \left(1 + a_{r1}\omega + a_{r2}\omega^2 + a_{r3}\mu^* + a_{r4}\mu^{*2} \right) \quad (2.117)$$

$$c_r = c_{r0} \left(1 + c_{r1}\omega + c_{r2}\omega^2 + c_{r3}\mu^* + c_{r4}\mu^{*2} \right) \quad (2.118)$$

The generalized Quartic EOS is extended to predict the behavior of the polar fluids. If the dipole moment of the fluid is zero, then the entire system is reduced to the non-polar fluid system. The values of the regressed coefficients are presented in Table 2.1.

Table 2.1: Quartic Equation of State Constants

Regressed coefficients		Regressed coefficients		Regressed coefficients	
a_{r0}	1.84713	X_{21}	0.14988	X_{52}	0.57743
a_{r1}	-0.05218	X_{22}	0.97848	X_{53}	0.41218
a_{r2}	1.06446	X_{23}	-0.01390	X_{54}	-0.10676
a_{r3}	-0.02730	X_{24}	0.02928	X_{61}	0.02581
a_{r4}	0.02048	X_{31}	-0.32379	X_{62}	-0.02700
c_{r0}	1.78336	X_{32}	1.84591	X_{63}	0.38327
c_{r1}	-1.29690	X_{33}	0.39338	X_{64}	-0.09008
c_{r2}	2.78945	X_{34}	-0.25483	X_{71}	-0.77357
c_{r3}	-0.07000	X_{41}	0.14833	X_{72}	-1.45342
c_{r4}	0.01188	X_{42}	-3.46693	X_{73}	-0.04725
e_{r0}	0.63189	X_{43}	-0.39170	X_{74}	-0.09669
e_{r1}	-0.81660	X_{44}	-0.01597	k_0	1.2865
e_{r2}	3.25246	X_{51}	0.11048	k_1	2.8225

2.3.8 Advantages and Disadvantages of Equation of state approach

In the Equation of State approach the definition of fugacity coefficient is used to describe both liquid and vapor phases through the application of single equation of state. The major advantage of this approach is its applicability over a wide range of pressures including critical and supercritical pressures. However, phase equilibrium calculations by these methods are rather lengthy except for a simple equation of state. Another problem associated with the use of the EOS technique is the insufficiency of information about the exact form of the EOS for mixtures, and the inaccuracy of the existing mixing rules for mixtures containing polar and hydrogen bonding components.

2.4 Mixing rules

Mixing rules used in the prediction of vapor-liquid equilibria of mixtures are as important as the equation of state itself. Quite often the classical van der Waals one fluid mixing rule with one binary interaction parameter was used. However, as the systems become complex in nature, the need for using better mixing rules grows enormously. It is highly unlikely that the performance of a new equation of state will be better, unless improved mixing rules are used (Tsonopoulos et al., 1985). This led to the proposal of many modifications to the existing classical van der Waals type of mixing rules.

Given below are some of the most widely used mixing rules for a large number of equations of state in order to calculate the mixture parameters.

2.4.1 van der Waals Mixing Rules

These are also called the classical mixing rules and are given by:

$$a = \sum_i^c \sum_j^c x_i x_j a_{ij} \quad (2.119)$$

$$b = \sum_i^c \sum_j^c x_i x_j b_{ij} \quad (2.120)$$

Where a is the energy parameter and b is the volume parameter, a_{ij} and b_{ij} are the cross terms i.e. the interaction terms when ($i \neq j$) whereas i and j represent the components (c).

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}) \quad (2.121)$$

$$b_{ij} = \left(\frac{b_{ii} + b_{jj}}{2} \right) (1 - l_{ij}) \quad (2.122)$$

Where k_{ij} and l_{ij} are the binary interaction parameters; l_{ij} being zero most of the times. When Eq. (2.122) is applied to Eq. (2.120) with $l_{ij} = 0$, it reduces to a linear term.

$$b = \sum_i^c x_i b_{ii} \quad (2.123)$$

The above vdW one fluid mixing rules are used for van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson equations of state with a single binary interaction parameter k_{ij} , ($l_{ij} = 0$).

2.4.2 Composition Dependent Mixing Rules

These mixing rules were first proposed by Huron and Vidal (1979) and Stryjek and Vera (1986) as modifications to the existing van der Waals mixing rules, to improve the vapor-liquid equilibrium calculations. Stryjek and Vera (1986) proposed the following mixing rules,

$$a = \sum_i^c \sum_j^c x_i x_j a_{ij} \quad (2.124)$$

$$b = \sum_i^c x_i b_{ii} \quad (2.125)$$

where the cross terms are same as those for the vdW but, with a change in the binary interaction parameter. Two binary interaction parameters k_{ij} and k_{ji} are used with composition dependence for a parameter. Stryjek and Vera (1986) proposed two different types of composition dependence for the interaction parameters.

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - x_i k_{ij} - x_j k_{ji}) \quad (2.126)$$

Eq. (2.126) is a Margules type cross term and

$$a_{ij} = \sqrt{a_{ii}a_{jj}} \left(1 - \frac{k_{ij}k_{ji}}{x_i k_{ij} + x_j k_{ji}} \right) \quad (2.127)$$

Eq. (2.127) is a Van Laar type cross term.

The above mentioned mixing rules are used for Peng-Robinson-Stryjek-Vera equation of state.

2.4.3 Conformal Solution van der Waals Mixing Rules

These mixing rules were proposed by Kwak and Mansoori (1986), and were used by Benmekki and Mansoori (1987, 1988). These mixing rules differ depending on the EOS used. For the PR EOS, when the temperature dependent term is expanded and re-written,

$$\begin{aligned} a(T, \omega) &= a(T_c)(1 + \kappa(1 - T_R^{1/2}))^2 \\ &= a(T_c)(1 + 2\kappa(1 - T_R^{0.5}) + \kappa^2(1 + T_R - 2T_R^{0.5})) \\ &= a(T_c)(\kappa + 1)^2 + a(T_c)\kappa^2 T_R - 2\kappa(\kappa + 1)a(T_c)T_R^{0.5} \\ &= c + dRT - 2\sqrt{cdRT} \end{aligned} \quad (2.128)$$

Where

$$c = a(T_c)(1 + \kappa)^2 \quad (2.129)$$

$$d = a(T_c) \frac{\kappa^2}{RT_c} \quad (2.130)$$

b is the same as it is in the PR EOS, leads to the following mixing rules.

$$b = \sum_i^c \sum_j^c x_i x_j b_{ij} \quad (2.131)$$

$$c = \sum_i^c \sum_j^c x_i x_j c_{ij} \quad (2.132)$$

$$d = \sum_i^c \sum_j^c x_i x_j d_{ij} \quad (2.133)$$

The cross terms or the combining rules are given by

$$b_{ij} = (1 - l_{ij})^3 \left(\frac{\frac{1}{b_{ii}^3} + \frac{1}{b_{jj}^3}}{2} \right) \quad (2.134)$$

$$c_{ij} = (1 - k_{ij})^3 \left(\frac{\frac{1}{b_{ii}^3} \frac{1}{b_{jj}^3}}{\frac{1}{b_{ii}^3} + \frac{1}{b_{jj}^3}} \right)^{\frac{1}{2}} b_{ij} \quad (2.135)$$

$$d_{ij} = (1 - m_{ij})^3 \left(\frac{d_{ii}^{\frac{1}{3}} + d_{jj}^{\frac{1}{3}}}{2} \right)^3 \quad (2.136)$$

Where, k_{ij} , l_{ij} , and m_{ij} are adjustable binary interaction parameters.

2.4.4 Wong – Sandler Mixing Rule

Wong and Sandler (1992) developed these mixing rules by equating the Helmholtz free energy at infinite pressure obtained by using an equation of state with that obtained from a liquid solution model (Activity coefficient model). Orbey and Sandler (1996) used it with different EOS to calculate VLE of some highly non-ideal systems. The mixing rules are given below:

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (2.137)$$

$$\frac{A_\gamma^{ex}}{CRT} = \frac{a}{bRT} - \sum_i x_i \frac{a_{ii}}{b_{ii} RT} \quad (2.138)$$

where $\left(b - \frac{a}{RT} \right)$ is the second virial coefficient obtained by the expansion of the van der Waals equation in virial form, A_γ^{ex} is the excess Helmholtz free energy obtained from the activity coefficient model, C is a constant specific to the EOS chosen. For the Peng–Robinson equation

$$C = [\ln(\sqrt{2} - 1)] / \sqrt{2} = -0.62323$$

The cross term in Eq. (2.137) is given by

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_{ii} - \frac{a_{ii}}{RT} \right) + \left(b_{jj} - \frac{a_{jj}}{RT} \right) \right] (1 - k_{ij}) \quad (2.139)$$

Any EOS can use these mixing rules but one has to calculate the excess Helmholtz free energy by using any one of the activity coefficient models mentioned previously in this chapter.

CHAPTER 3

LITERATURE REVIEW

Many attempts were made in the recent past to determine the VLE of various systems and to obtain the model parameters by using experimental VLE data. The work done by the Thermodynamic Data Center (TDC) at Warsaw, Poland (Marczynski 1988) is worth appreciating as they published 6 volumes by collecting the experimental data from the world literature.

The TDC data bank contains experimental data of thermophysical properties for pure substances as well as for mixtures. Data for pure substances is primarily collected from Thermodynamics Research Center (TRC) at The Texas A&M University, USA, while data for binary and ternary mixtures is predominantly from TDC. Vapor-liquid equilibrium data is the most essential part of this collection.

At TDC experimental data is collected on the basis of the open world literature and evaluated at the following tests: primary experimental data, selected data, recommended data and parameters of selected equation. Selected and recommended data are prepared after critical evaluation, which includes correlations and thermodynamic consistency tests. Parameters for selected equation are calculated mainly for selected and recommended data over a given range of temperature.

The first volume contains selected and correlated data for binary mixtures containing C₅ - C₆ hydrocarbons combined with C₅-C₂₀ hydrocarbons. The second volume contains the data for binary mixtures containing C₇-C₁₄ hydrocarbons combined with C₇-C₁₈ hydrocarbons, while the third volume contains selected and correlated data for binary mixtures containing C₁-C₁₂ alcohols combined with C₅-C₁₈ aliphatic hydrocarbons. The fourth volume contains the data for binary mixtures containing C₁-C₁₀ alcohols combined with C₅-C₁₀ non-aliphatic hydrocarbons. The fifth volume deals with the C₁-C₁₂ alcohols and C₃-C₁₀ ethers binary mixtures. The sixth volume contains selected and correlated data for binary mixtures containing C₃-C₁₈ esters combined with C₁-C₆ alcohols and C₄-C₂₀ hydrocarbons.

With the growing importance of refrigerants, the need for the VLE of the refrigerant mixtures was stressed on and many researchers were worked in this area. They also tried

to obtain the parameters required for various prediction methods by fitting the experimental data. Some of those works have been discussed in the subsequent paragraphs. Eva Fransson et al. (1992) used a constant -volume cell to determine vapor-liquid equilibria by the static method for the binary systems n-pentane + chlorodifluoromethane (R22) or + 1,1, -difluoroetane (R152a). They carried out the measurements between 303 and 383 K and between 0.3 and 4.4 MPa for different compositions of the mixtures. From a knowledge of overall composition, pressure and temperature they calculated the vapor and liquid compositions using the Soave-Redlich-Kwong equation of state together with an interaction parameter. They concluded that the variation of binary interaction parameter with the temperature for these systems is negligible.

The experimental data for vapor liquid equilibrium for the three non-azeotropic mixtures HCFC22/CFC114 ($\text{CHClF}_2/\text{C}_2\text{Cl}_2\text{F}_4$), HCFC22/HCFC142b ($\text{CHClF}_2/\text{C}_2\text{H}_3\text{ClF}_3$) and HCFC22/HFC152a ($\text{CHClF}_2/\text{C}_2\text{H}_4\text{F}_2$) along with the vapor pressures for the pure components were determined by Krister et al. (1993). They compared the experimental and calculated data and presented the deviations. They used different models for this purpose and the models were Lee-kesler and Carnahan-Starling-de santis of EOS category and activity coefficient model by Wilson. Interaction parameters were fitted from experimental data to the mixing rules proposed to the two equations of state and the activity coefficient parameters were determined. All three methods studied gave good conformity with experimental data for the three mixtures examined.

Michael Kleiber (1994) obtained the VLE for the binary mixtures propylene-R12, propylene-R22, propylene-R152a, propylene-R13, propylene-R23, propylene-R134a, propylene-R115, propylene-R13B1, propylene-R114, propylene-R116, R134a-R12, R134a-R152a, R134a-R116, R134a-R12, and R134a-propane at temperatures between 251 and 298 K and pressure up to 2 MPa. He showed the consistency of the data by a maximum-likelihood method. He also correlated the data by generalized forms of various EOS such as Peng-Robinson (PR), Peng-Robinson-Stryjeck-vera (PRSV), Redlich-kwong-soave (RKS) and Lee-Kesler-Plocker (LKP) along with appropriate mixing rules. These EOS were fitted to the experimental data by optimizing the binary interaction parameters. Considering the fitting rules, The LKP equation seems to perform worse than the others, especially for azeotropic mixtures like propylene-R152a, propylene-R115,

propylene-R134a, R134a-propane R134a-R12. The PR, RKS and PRSV equations yield similar results in each case. The system R134a-R116 was described significantly worse than the other mixtures. Only the PRSV equation with the van laar type was able to describe it satisfactorily. This mixing rule is, of course, superior to the others, because it has two adjustable parameters instead of only one, but usually it gives only slightly better results than normal vdW mixing rule.

Hideo Nishiumi et al. (1995) measured VLE data for the systems-chlorodifluoromethane (HCFC22) - dichlorodifluoromethane (CFC12) over the temperature range 348.81 K to 374.14 K and HCFC22 - dichlorotrifluoroethane (HCFC123) from 313.48 K to 414.57 K, and vapor pressures and the critical properties of their components. Binary interaction parameters of an extended BWR equation of state for the systems containing fluorocarbons including the above mentioned systems were correlated as quadratic equations of temperature. Using the parameters obtained from the VLE measurements they estimated the coefficients of performance (COP) for these binary refrigerant mixtures and found that about 17% energy would be saved for the system HCFC22-HCFC123 as a mixture-refrigerant in comparison with HCFC22.

Masanao Kobayashi and Hideo Nishiumi (1998) measured the VLE for the pure, binary and ternary systems containing difluoromethane (HFC32), pentafluoroethane (HFC125) and 1,1,1,2-tetrafluoroethane (HFC134a). The binary interaction parameters were determined from the VLE data by using extended BWR equation of state. Using the binary parameters, they predicted the VLE data for a ternary system at 333.15 K and 2.43 MPa, which is in excellent agreement.

The Isothermal VLE data of the binary system of difluoromethane (HFC-32) + 1,1,1-trifluoroethane (HFC-143a) were obtained in the temperature range from 263.15 K to 313.15 K by Chang Nyeon Kim and Young Moo Park (2000). They measured the temperature, pressure, and compositions of the liquid and vapor phases with a circulation type apparatus. The experimental data were correlated with the Carnahan-Starling-De Santis (CSD), Peng-Robinson, and Redlich-Kwong-Soave equations of state. It is evident that the binary interaction parameter for the CSD equation of state increase slightly as the temperature increases. On the other hand, the binary interaction parameters for both the PR and RKS equations of state decrease as the temperature increases. The binary interaction parameter for the RKS equation has the larger temperature dependence than

those for the CSD and PR equations of state. The average deviation between the measured pressures and the calculated results from the CSD equation of state is about 0.29% and that from the PR equation of state it is about 0.45%. The average deviation from the RKS equation of state is about 0.70%. As a result, they concluded that the CSD equation of state correlates the experimental data better than the PR and RKS equations of state.

Lim et al. (2000) measured the Isothermal VLE data of the binary mixtures of trifluoromethane (HFC-23) + isobutene (R600a) and 1,1,1-trifluoroethane (HFC-143a) + isobutene at 283.15 and 293.15 K and at 323.15 and 333.15 K, respectively. They carried out the experiment in a circulation-type equilibrium apparatus with the provision for measurement of temperature, pressure, and the compositions of the liquid and vapor phases. They correlated the experimental data with the Peng-Robinson equation of state using the Wong and Sandler mixing rules. When NRTL model was used along with the Wong –Sandler mixing rule, the average deviations of pressure are 0.644% for the HFC-23 + Isobutane system and 0.30% for the HFC-143a + isobutene system and those of the vapor phase compositions are 0.0066 for the HFC-23 + Isobutane system and 0.0058 for the HFC-143a + isobutene system. After examining the results they concluded that the values calculated with the Peng-Robinson equation of state and Wong sandler mixing rules are comparatively in good agreement with experimental data.

CHAPTER 4

PREDICTION OF VLE DATA

The purpose of phase-equilibrium thermodynamics is to predict the conditions (T , P , composition) prevailing when two or more phases are in equilibrium. The thermodynamic equations which determine the state of equilibrium between vapor and liquid phases are $T^l = T^v$ (T is constant), $P^l = P^v$ (P is constant), and $f_i^l = f_i^v$. To find the conditions which satisfy these equations, it is necessary to have a method for evaluating the fugacity (f_i) of each component in both vapor and liquid phases. This can be done using the basic thermodynamic equation for calculating the fugacity coefficient (ϕ_i^l or ϕ_i^v).

The fugacity coefficient can be obtained by using the relation

$$\ln\left(\frac{f_i}{y_i P}\right) = \ln \phi_i = \frac{1}{RT} \int_0^P \left(\bar{v}_i - \frac{RT}{P} \right) dP \quad (4.1)$$

Where $\bar{v}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j}$ = the partial molar volume.

Or,

$$\ln\left(\frac{f_i}{y_i P}\right) = \ln \phi_i = \frac{1}{RT} \int_v^\infty \left(\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right) dV - \ln Z \quad (4.2)$$

The solution to the phase-equilibrium problem is provided completely by either one of these equations together with an EOS and the equations of phase-equilibrium. Eq. (4.1) is used when the EOS is given in volume explicit form ($V = V_V(P, T, n_1, n_2, \dots)$) whereas Eq. (4.2) is used when the EOS is in the pressure explicit form ($P = P_V(V, T, n_1, n_2, \dots)$). Most of the EOS are pressure explicit type. To use an EOS, one must transform the EOS in molar form to a total form first. When one is to calculate the fugacity of component i in the mixture at a specified T , P , and composition, differentiate the EOS w.r.t n_i , and substitute in Eq. (4.2) to get the result.

There are basically four classes of VLE problems:

BUBLP: Calculate $\{y_i\}$ and P , given $\{x_i\}$, T .

DEWP: Calculate $\{x_i\}$ and P , given $\{y_i\}$, T .

BUBLT: Calculate $\{y_i\}$ and T , given $\{x_i\}$, P .

DEWT: Calculate $\{x_i\}$ and T , given $\{y_i\}$, P .

The problems of engineering interest generally deal with *BUBLP* or *DEWP*. In order to correlate the experimental data, choice of the model to calculate the fugacity coefficients and the determination of the best or the most representative parameters for the model are the most important steps. The models in this chapter are based on the PR EOS and Quartic EOS, each combined separately with *vdW* mixing rules and composition dependent two parameter mixing rules.

4.1 Model I: PR EOS with van der Waals one fluid mixing rules

The PR EOS expressed on a total basis, in pressure explicit form, is

$$P = \frac{n_t RT}{V - n_t b} - \frac{n_t^2 a(T, \omega)}{V(V + n_t b) + n_t b(V - n_t b)} \quad (4.3)$$

where $V = vn_t$ and

n_t = total number of moles

Eq. (4.3) when differentiated on molar basis and substituted in Eq. (4.2) with the use of van der Waals one fluid mixing rules (Eqs. (2.119) through (2.123)) gives the following expression for the fugacity coefficient.

$$\ln \phi_i = (Z - 1)B'_i - \ln(Z - B) - \frac{A}{2\sqrt{2}B}(A'_i - B'_i) \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (4.4)$$

where

$$A'_i = \frac{1}{a} \left(2a_{ii}^{0.5} \sum_j^c x_j a_{jj}^{0.5} (1 - k_{ij}) \right) \quad (4.5)$$

$$\dot{B}'_i = \frac{b_{ii}}{b} \quad (4.6)$$

$$A = \frac{aP}{R^2 T^2} \quad (4.7)$$

$$B = \frac{bP}{RT} \quad (4.8)$$

Eq. (4.4) is used to calculate the fugacity coefficient of either liquid or vapor phase, by using the appropriate compressibility factor and the composition.

4.2 Model II: PR EOS with composition dependent two parameter mixing rules

The PR EOS in the pressure explicit form expressed on a total basis is,

$$P = \frac{n_t RT}{V - n_t b} - \frac{n_t^2 a(T, \omega)}{V(V + n_t b) + n_t b(V - n_t b)} \quad (4.3)$$

where $V = v n_t$ and

n_t = total number of moles

Eq. (4.3), when used properly in Eq. (4.2), with the use of vdW one fluid and Margules type (Stryjek and Vera 1986) mixing rules (Eqs. (2.119), (2.123), and (2.124)) gives the following expression for fugacity coefficient.

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left(\frac{\bar{a}_i}{a} + 1 - \frac{b_i}{b} \right) \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (4.9)$$

where

$$\bar{a}_i = 2 \left(\sum x_j \sqrt{a_{ii} a_{jj}} (1 - x_i k_{ij} - x_j k_{ji}) + x_i x_j^2 \sqrt{a_{ii} a_{jj}} (k_{ji} - k_{ij}) \right) \quad (4.10)$$

$$A = \frac{aP}{R^2 T^2} \quad (4.7)$$

$$B = \frac{bP}{RT} \quad (4.8)$$

Eq. (4.9) is used to calculate the fugacity coefficients of both vapor and liquid phases.

4.3 Model III: Quartic EOS with van der Waals one fluid mixing rules

The Quartic EOS in the pressure explicit form expressed on a total basis is,

$$P = \frac{n_t RT}{(V - n_t k_0 \beta)} + \frac{n_t^2 \beta k_t RT}{(V - n_t k_0 \beta)^2} - \frac{n_t^2 a V + n_t^3 k_0 \beta c}{V(V + n_t e)(V - n_t k_0 \beta)} \quad (4.11)$$

where $V = v n_t$, and

n_t = total number of moles

Eq. (4.11) when differentiated on molar basis and substituted in Eq. (4.2) with the use of van der Waals one fluid mixing rules (Eqs. (2.119) through (2.123)) gives the following expression for the fugacity coefficient.

$$\ln \hat{\phi}_i = L + \frac{1}{RT} [Q \ln z + N \ln(z + E_1) + M \ln(z - E_2)] - \ln(z - E_2) \quad (4.12)$$

where

$$L = \frac{k_0 \beta_i}{(v - k_0 \beta)} + \frac{k_1 \beta_i v}{(v - k_0 \beta)^2} + \frac{k_1 \beta}{(v - k_0 \beta)} - \frac{1}{RT} \left[\frac{a}{(k_0 \beta + e)} \left\{ \frac{k_0 \beta_i}{(v - k_0 \beta)} + \frac{e_i}{(v + e)} \right\} \right] + \frac{1}{RT} \left[\frac{c}{(k_0 \beta + e)} \left\{ \frac{k_0 \beta_i e_i}{e(v + e)} - \frac{k_0 \beta_i}{(v - k_0 \beta)} \right\} \right] \quad (4.13)$$

$$M = \left[\frac{2a'_i}{(k_0 \beta + e)} - \frac{\{a(k_0 \beta_i + e_i) + c(e_i - k_0 \beta k_0 \beta_i / e)\}}{(k_0 \beta + e)^2} + \frac{k_0 \beta 2c'_i + k_0 \beta_i c}{k_0 \beta (k_0 \beta + e)} - \frac{k_0 \beta_i c}{k_0 \beta e} \right] \quad (4.14)$$

$$N = \left[-\frac{2a'_i}{(k_0 \beta + e)} + \frac{\{a(k_0 \beta_i + e_i) + c(e_i - k_0 \beta k_0 \beta_i / e)\}}{(k_0 \beta + e)^2} + \frac{k_0 \beta 2c'_i + k_0 \beta_i c}{k_0 \beta (k_0 \beta + e)} - \frac{k_0 \beta_i c}{k_0 \beta e} \right] \quad (4.15)$$

$$Q = \left[-\frac{k_0 \beta 2c'_i + k_0 \beta_i c}{k_0 \beta e} + \frac{c(\beta_i e + e_i \beta)}{\beta e^2} \right] \quad (4.16)$$

$$E_1 = \frac{Pe}{RT} \quad (4.17)$$

$$E_2 = \frac{Pk_o\beta}{RT} \quad (4.18)$$

$$a'_i = \sum x_j \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (4.19)$$

$$c'_i = \sum x_j \sqrt{c_{ii} c_{jj}} (1 - k_{ij}) \quad (4.20)$$

Eq. (4.12) is used to calculate the fugacity coefficients of both vapor and liquid phases.

4.4 Model IV: Quartic EOS with composition dependent two parameter mixing rules

The Quartic EOS in the pressure explicit form expressed on a total basis is,

$$P = \frac{n_t RT}{(V - n_t k_o \beta)} + \frac{n_t^2 \beta k_t RT}{(V - n_t k_o \beta)^2} - \frac{n_t^2 a V + n_t^3 k_o \beta c}{V(V + n_t e)(V - n_t k_o \beta)} \quad (4.11)$$

where $V = v n_t$ and

n_t = total number of moles

Eq. (4.11), when used properly in Eq. (4.2), with the use of vdW one fluid and Margules type (Stryjek and Vera 1986) mixing rules (Eqs. (2.119), (2.123), and (2.124)) gives the following expression for fugacity coefficient.

$$\ln \hat{\phi}_i = L + \frac{1}{RT} [Q \ln z + N \ln(z + E_1) + M \ln(z - E_2)] - \ln(z - E_2) \quad (4.21)$$

where

$$L = \frac{k_o \beta_i}{(v - k_o \beta)} + \frac{k_1 \beta_i v}{(v - k_o \beta)^2} + \frac{k_1 \beta}{(v - k_o \beta)} - \frac{1}{RT} \left[\frac{a}{(k_o \beta + e)} \left\{ \frac{k_o \beta_i}{(v - k_o \beta)} + \frac{e_i}{(v + e)} \right\} \right] + \frac{1}{RT} \left[\frac{c}{(k_o \beta + e)} \left\{ \frac{k_o \beta_i e_i}{e(v + e)} - \frac{k_o \beta_i}{(v - k_o \beta)} \right\} \right] \quad (4.22)$$

$$M = \left[\frac{2a''_i}{(k_o \beta + e)} - \frac{\{a(k_o \beta_i + e_i) + c(e_i - k_o \beta k_o \beta_i / e)\}}{(k_o \beta + e)^2} + \frac{k_o \beta 2c''_i + k_o \beta_i c}{k_o \beta (k_o \beta + e)} - \frac{k_o \beta_i c}{k_o \beta e} \right] \quad (4.23)$$

$$N = \left[-\frac{2a''_i}{(k_o \beta + e)} + \frac{\{a(k_o \beta_i + e_i) + c(e_i - k_o \beta k_o \beta_i / e)\}}{(k_o \beta + e)^2} + \frac{k_o \beta 2c''_i + k_o \beta_i c}{k_o \beta (k_o \beta + e)} - \frac{k_o \beta_i c}{k_o \beta e} \right] \quad (4.24)$$

$$Q = \left[-\frac{k_o \beta 2c''_i + k_o \beta_i c}{k_o \beta e} + \frac{c(\beta_i e + e_i \beta)}{\beta e^2} \right] \quad (4.25)$$

$$E_1 = \frac{Pe}{RT} \quad (4.26)$$

$$E_2 = \frac{Pk_o \beta}{RT} \quad (4.27)$$

$$a''_i = \sum x_j \sqrt{a_{ii} a_{jj}} (1 - x_i k_{ij} - x_j k_{ji}) + x_i x_j^2 \sqrt{a_{ii} a_{jj}} (k_{ji} - k_{ij}) \quad (4.28)$$

$$c''_i = \sum x_j \sqrt{c_{ii} c_{jj}} (1 - x_i k_{ij} - x_j k_{ji}) + x_i x_j^2 \sqrt{c_{ii} c_{jj}} (k_{ji} - k_{ij}) \quad (4.29)$$

Eq. (4.21) is used to calculate the fugacity coefficients of both vapor and liquid phases.

4.5 VLE Calculations

The most important step of calculating the fugacity coefficients (ϕ_i^l or ϕ_i^v) is carried out by using the four models described. This requires Z^l , the liquid phase compressibility factor or Z^v , the vapor phase compressibility factor. These are obtained by solving the EOS which is expressed in terms of the compressibility factor Z .

For PR EOS, we can obtain the Z^l and Z^v by solving the following cubic EOS which is expressed in terms of the compressibility factor Z .

$$Z^3 + (B - 1)Z^2 + (A - 3B^2 - 2B)Z + (B^2 + B^3 - AB) = 0 \quad (4.30)$$

where

$$A = \frac{aP}{R^2 T^2} \quad (4.7)$$

$$B = \frac{bP}{RT} \quad (4.8)$$

$$Z = \frac{PV}{nRT} \quad (4.31)$$

Eq. (4.30) when solved gives three roots. There are two possibilities; either all the three roots are real or only one real root (remaining two being complex). When there are three real roots, the smallest root is the liquid phase compressibility factor and the largest root

is the vapor phase compressibility factor, intermediate root being meaningless. If it is only one root, it is taken either as the liquid phase or vapor phase compressibility factor depending on the calculations.

For Quartic EOS the Z^l and Z^v are obtained by solving the following quartic EOS which is expressed in terms of the compressibility factor Z .

$$Z^4 + q_3 Z^3 + q_2 Z^2 + q_1 Z + q_0 = 0 \quad (4.32)$$

where

$$q_3 = \left[-2k_0\beta + e - \frac{RT}{P} \right] \frac{P}{RT} \quad (4.33)$$

$$q_2 = \frac{P}{RT} \left[(\beta(k_0 + k_1) - e) + \left(\frac{P}{RT} \right) k_0 \beta (k_0 \beta - e) \right] + \frac{aP}{(RT)^2} \quad (4.34)$$

$$q_1 = \frac{P^3 e}{(RT)^3} \left[(k_0 \beta)^2 + \frac{RT\beta}{P} (k_0 + k_1) \right] + \left(\frac{P}{RT} \right)^3 \left[\left(k_0 \beta \frac{(c-a)}{P} \right) \right] \quad (4.35)$$

$$q_0 = -\frac{ck_0^2 \beta^2 P^3}{(RT)^4} \quad (4.36)$$

On solving Eq. (4.32) one obtains four values of Z , one of which is always negative. Among the three positive values of Z , the highest value of Z corresponds to vapor phase (Z^v) while the smallest value corresponds to liquid phase (Z^l). The intermediate value of Z has no physical significance. Substituting Z^v or Z^l values in Eq. (4.12) or Eq. (4.21) one can get $\hat{\phi}_i^v$ or $\hat{\phi}_i^l$

4.6 Data Reduction

As mentioned earlier, there are two important steps i) model selection and ii) evaluation of the best parameters for the model. This needs reduction of the VLE data. In this work, only P - x - y data (given T and x_i) is used. Binary interaction parameters in the models used are obtained by optimizing an objective function. The objective function

used in this work is a sum of two functions namely a pressure (OFP) and a vapor phase composition (OFY) function (Benmekki et al., 1987). For the optimization of this objective function, a function ‘*fmins*’ of the ‘Matlab’, which uses a Nelder Mead Simplex algorithm is used.

$$OF = OFP + OFY \quad (4.37)$$

where

$$OFP = \sum_{i=1}^N \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)_i^2 \quad (4.38)$$

$$OFY = \sum_{i=1}^N \left(\frac{y_{1\text{exp}} - y_{1\text{cal}}}{y_{1\text{exp}}} \right)_i^2 \quad (4.39)$$

where, P_{exp} , P_{cal} are experimental and calculated pressure respectively, $y_{1\text{exp}}$, $y_{1\text{cal}}$ are experimental and calculated vapor phase compositions of component 1, and N is the number of data points.

At the optimum values of the binary interaction parameters, the average absolute deviations in pressure and composition are calculated from the relations,

$$\frac{\Delta P}{P} = \left(\frac{OFP}{N} \right)^{\frac{1}{2}} \quad (4.40)$$

$$\frac{\Delta y_1}{y_1} = \left(\frac{OFY}{N} \right)^{\frac{1}{2}} \quad (4.41)$$

The codes employed in this work are given in the Appendix A for all the four models. The algorithm used in VLE calculations is given in Fig. (4.1) and Fig. (4.2) and (4.3) show the subroutines for PR and Quartic EOS, respectively.

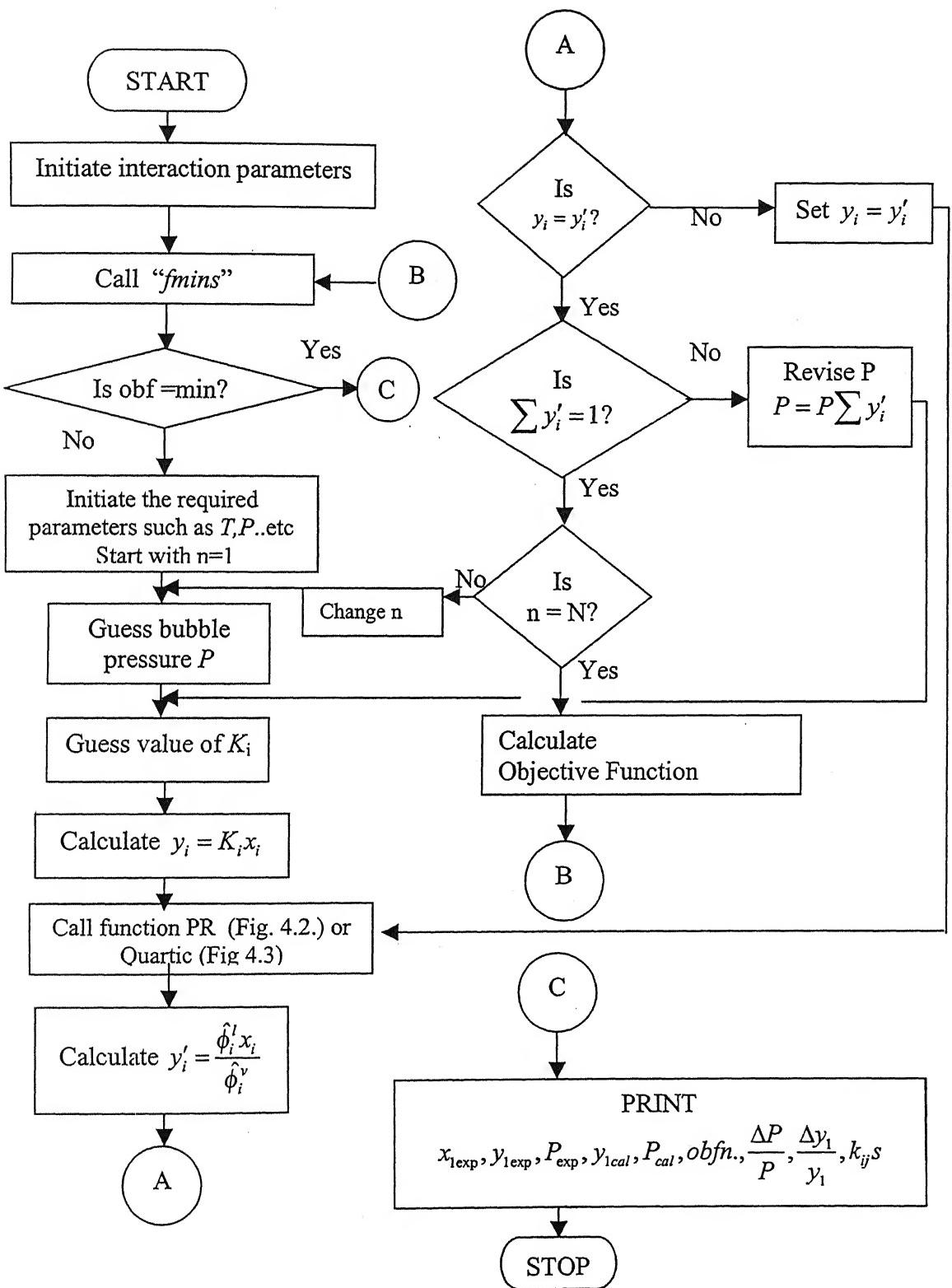


Fig 4.1. Algorithm for VLE Prediction.

Subroutine PR

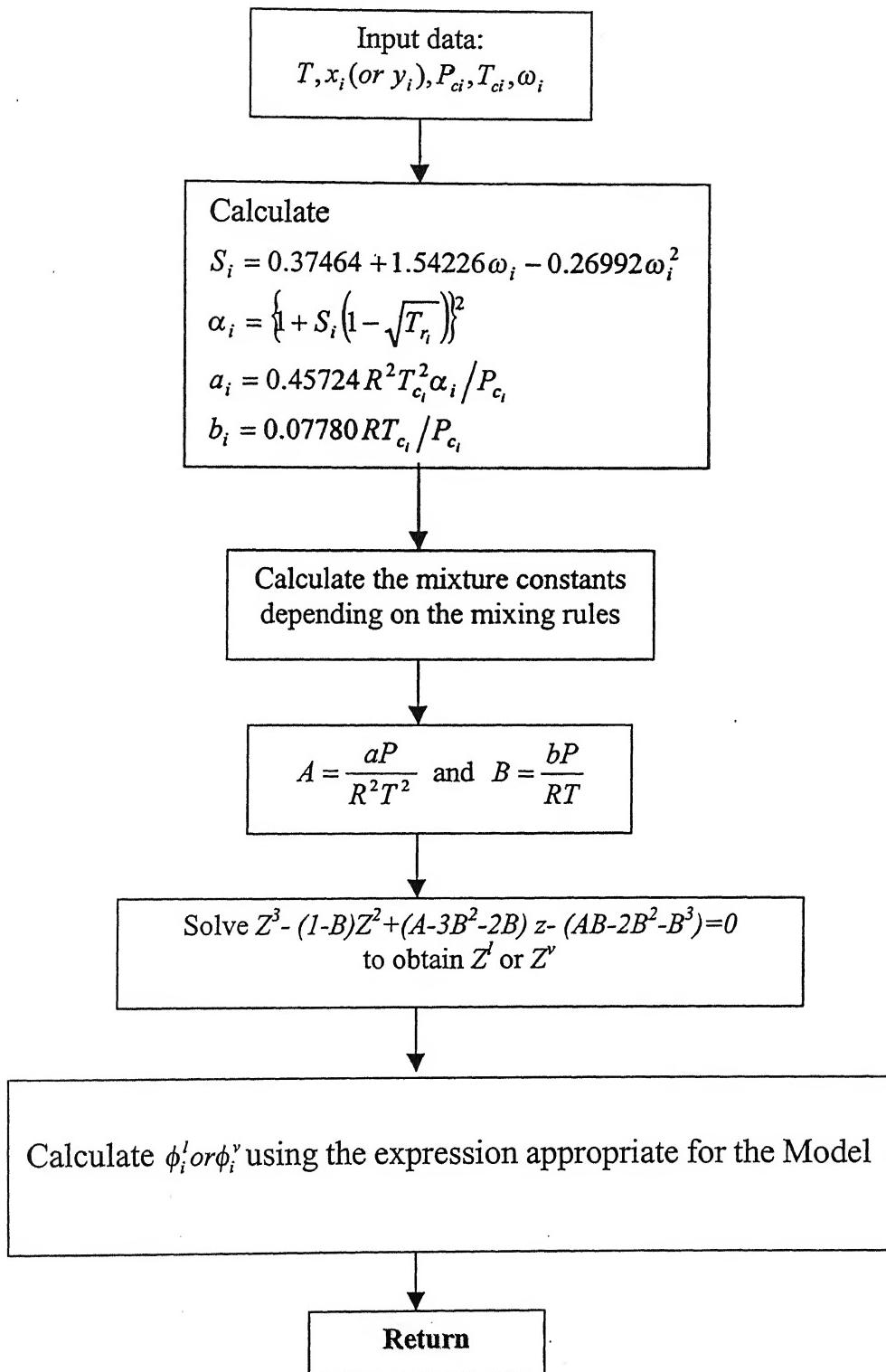


Fig 4.2 Subroutine for Peng-Robinson equation of state.

Subroutine Quartic

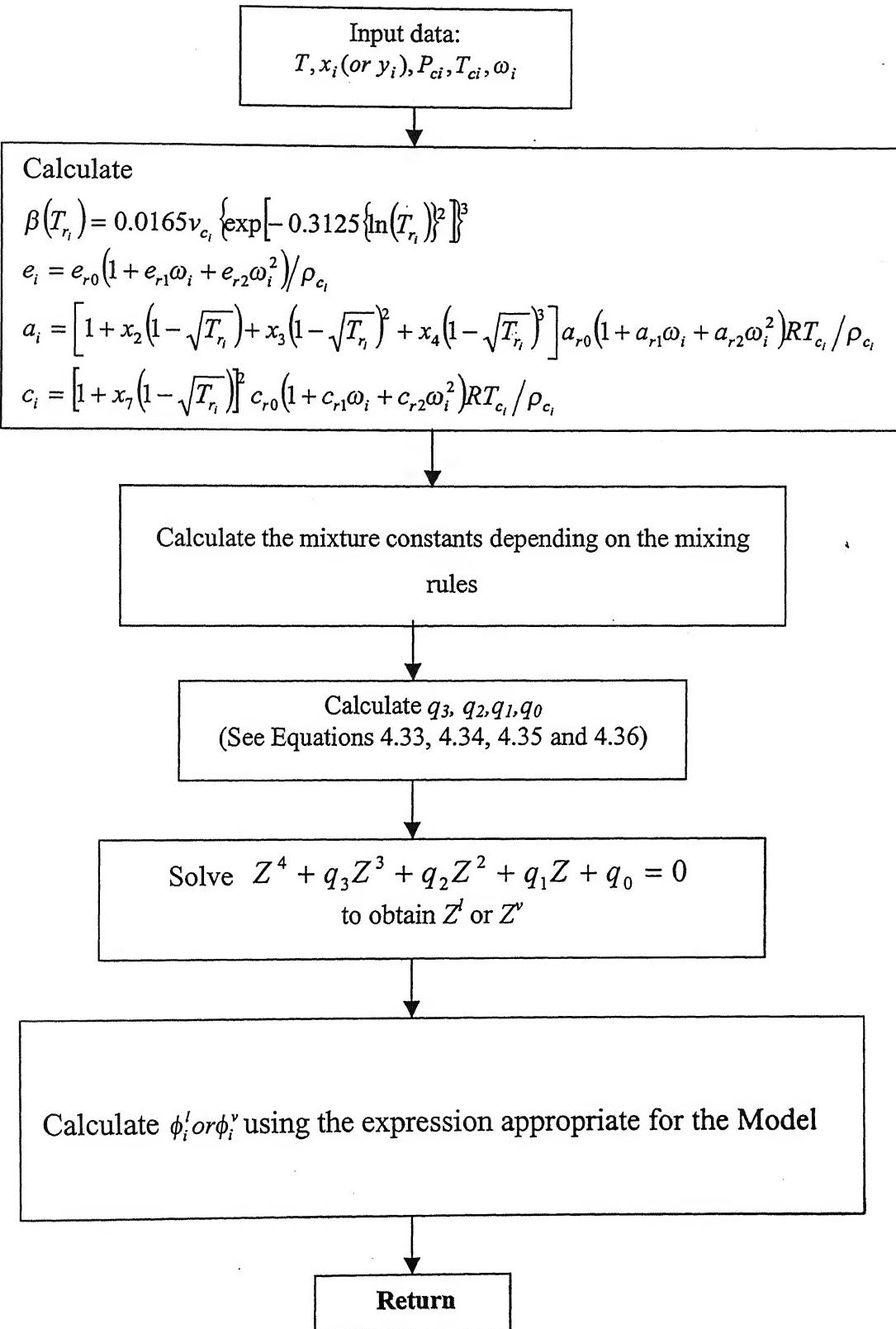


Fig 4.3 Subroutine for Quartic equation of state

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Results

The results obtained from the four models are presented in this section. In the first two models Peng-Robinson EOS was used, and in the next two models Quartic EOS was used. The results obtained with these four models are compared to ascertain the best model. A total of 33 binary systems at different temperatures were studied. These systems are classified into 7 different classes, such as alcohol/alcohol, alcohol/hydrocarbon, hydrocarbon/hydrocarbon, hydrocarbon / chlorofluorocarbon (CFC), hydrocarbon/hydro chlorofluorocarbon (HCFC), hydrocarbon /hydro fluorocarbon (HFC) and HFC/HFC. Table (5.1) lists all the systems considered in this study. The critical constants, acentric factors and the dipole moments of the compounds (Reid et al. 1987) are listed in Table (5.2). The systems range from non-polar/non-polar (hydrocarbon/hydrocarbon) to highly polar/polar (HFC/HFC). Only isothermal VLE (BUBLP) data is considered. The objective function used for the estimation of the optimum binary interaction parameters is a more rigorous one, which is a sum of the deviations in both pressure and vapor phase composition.

The average absolute deviations in pressure and vapor-phase composition along with the optimum objective function (OF) of the all systems studied are presented in Table (5.3). The binary interaction parameters for all the four models at the optimized objective function are presented in Table (5.4). The pressure (P) and vapor-phase composition (y_i) at the optimum binary interaction parameter values of one system for each class at one temperature are presented in Tables (5.5) - (5.11). The minimum percent deviations observed for pressure and vapor-composition are 0.12 and 0.35 respectively and the corresponding maximum values are 40.92 and 25.26. The results for Methanol/Ethanol system are presented in Fig. 5.1. As the predicted results are in close agreement with the experimental values the graphical representation for other systems is omitted.

5.2 Discussion

In this work thirty three systems of different classes at different temperatures have been studied using the PR EOS and Quartic EOS. Two types of mixing rules namely vdW mixing rules and composition dependent mixing rule, with Margules type cross term, are used. The systems studied in this work range from nonpolar systems (Pentane/Benzene, Pentane/Decane, Benzene/hexane, Benzene/Heptane, Benzene/Octane) to highly polar systems (R32/R143a). The results obtained indicate that Model 2 i.e. PR EOS with composition dependent mixing rules yields better results for most of the systems. For some systems, the Model 2 is predicting the VLE data that is as good as the remaining models.

The performances of the models are different for different classes of systems considered in this work. For alcohol/alcohol class of systems (Methanol/Propanol, Methanol/1-Butanol, Ethanol/1-butanol), which are polar in nature, the Model 4 i.e. Quartic EOS with composition dependent mixing rules predicted the VLE data better than the other models. But for Methanol/Ethanol system, the VLE data obtained by the Model 4 is as good as that obtained by the Model 2.

For Alcohol/Hydrocarbon systems, the VLE data obtained by the Model 2 i.e. PR EOS with composition dependent mixing rules is better than that by other models. But for the systems, which are having 1-Butanol as of the component (Butanol/Benzene, Butanol/Cyclohexane), the VLE data obtained by Model 4 is better than that by other models. For hydrocarbon/hydrocarbon systems of class three, which are non polar in nature Model 2 is as good as Model 4. But for those systems containing cyclohexane or Toluene, which are slightly polar in nature as one of the component of the system (cyclohexane/Hexane, Toluene/heptane, Toluene/octane, Toluene/Decane) the VLE data obtained by Model 4 is slightly better than Model 2.

For HC/CFC class systems (Propylene/R12, Propylene/R13, Propylene/R115) the VLE data obtained by Model 4 is as good as that obtained by Model 2. But in general Model 2 is preferable because of its ease in use. For HC/HCFC class of systems (Propylene/R22, Propylene/R142b) the Model 2 gave better results than other models. For HC/HFC class of systems (Propylene/R23, Propylene/R152a) the VLE data obtained by the Model 2 is better than that obtained by other models. For HFC/HFC class of

system (R32/R143a) the Model 2 gave good results. However Model 4 is also **equally** good for this system.

This study indicates that two parameter composition dependent mixing **rules** are better than the conventional vdW mixing rules for both PR EOS and Quartic EOS. Also this study indicates that the well known PR EOS displays better abilities in general as compared to the new Quartic EOS for nonpolar systems and refrigerant mixtures. But for the polar systems the Quartic EOS gave good results and for polar/nonpolar systems it's results are comparable to the results obtained by PR EOS.

Table.5.1: List of systems studied and the corresponding temperatures

S.No	SYSTEM	TEMPERATURE (K)
1	Methanol (1)/ Ethanol (2)	298.15
2	Methanol (1)/ Propanol (2)	333.17
3	Methanol (1)/ 1-Butanol (2)	298.15
4	Ethanol (1) / 1-Butanol (2)	323.15, 343.15, 363.15, 383.15, 403.15
5	Methanol (1)/Benzene (2)	308.15, 318.15, 328.15
6	Methanol (1)/Toluene (2)	318.15
7	Ethanol (1)/Benzene (2)	298.15, 318.15, 323.15, 328.22
8	Ethanol (1)/Cyclohexane (2)	273.15, 283.15, 293.15, 298.15, 303.15, 323.15
9	Ethanol (1)/Toluene (2)	308.15, 318.15, 328.15, 333.15
10	1-Propanol (1)/Benzene (2)	318.15, 328.15, 348.15
11	1-Propanol (1)/Cyclohexane (2)	323.01, 328.15, 338.15
12	1-Butanol (1)/Benzene (2)	298.15, 318.15
13	1-Butanol (1)/Cyclohexane (2)	298.15, 318.15, 323.15, 343.15
14	1-Butanol (1)/Toluene (2)	333.31, 343.40, 353.44, 373.15
15	Pentane (1)/Benzene (2)	308.15, 313.15, 318.15, 323.15
16	Pentane (1)/Decane (2)	317.70, 333.70
17	Benzene (1/-Hexane (2)	298.15, 333.15
18	Benzene (1)/Cyclohexane (2)	283.15, 298.15, 303.15, 313.15, 323.15, 333.15, 343.15, 403.15, 413.15, 423.15
19	Benzene (1)/Heptane (2)	293.15, 318.15, 328.15, 333.15, 353.15, 413.15
20	Benzene (1)/Toluene (2)	313.15, 334.15
21	Benzene (1)/Octane (2)	328.15, 338.15, 348.15
22	Cyclohexane (1)/Hexane (2)	298.15, 308.15, 343.15
23	Toluene (1)/Decane (2)	373.5, 383.6
24	Toluene (1)/Heptane (2)	303.15, 328.15
25	Toluene (1)/Octane (2)	333.15
26	Propylene (1)/R12 (2)	258.00, 263.00, 268.00, 273.00, 278.00, 283.00
27	Propylene (1)/R13 (2)	251.00, 273.00
28	Propylene (1)/R115 (2)	251.00, 275.00, 298.00
29	Propylene (1)-R22 (2)	258.00, 263.00, 268.00, 273.00, 278.00, 283.00
30	Propylene (1)/R142b (2)	268.00, 278.00, 288.00, 298.00
31	Propylene (1)/R23 (2)	251.00, 265.00
32	Propylene (1)/R152a (2)	255.00, 265.00, 275.00, 285.00

Table 5.1a: Source of Experimental data for the Refrigerant mixtures

S.No	System	Source
1	Propylene (1)/R12 (2)	Michael Kleiber (1994)
2	Propylene (1)/R13 (2)	Michael Kleiber (1994)
3	Propylene (1)/R115 (2)	Michael Kleiber (1994)
4	Propylene (1)-R22 (2)	Michael Kleiber (1994)
5	Propylene (1)/R142b (2)	Lim et al. (1999)
6	Propylene (1)/R23 (2)	Michael Kleiber (1994)
7	Propylene (1)/R152a (2)	Michael Kleiber (1994)
8	R32 (1)/R143a (2)	Chang Nyeon Kim et al. (2000)

Table 5.2. Properties of the compounds

S.No	Compound Name	T _C (K)	P _C (bar)	V _C (cm ³ /mol)	ω	μ (debye)
1	Methanol	512.6	80.9	118.0	0.556	1.70
2	Ethanol	513.9	61.4	167.1	0.644	1.70
3	Propanol	536.8	51.7	219.0	0.623	1.70
4	Butanol	563.1	44.2	275.0	0.593	1.80
5	Benzene	562.2	48.9	259.0	0.212	0.00
6	Toluene	591.8	41.0	316.0	0.263	0.40
7	Cyclohexane	553.5	40.7	308.0	0.212	0.30
8	Heptane	540.3	27.4	432.0	0.349	0.00
9	Hexane	507.5	30.1	370.0	0.299	0.00
10	Pentane	469.7	33.7	304.0	0.251	0.00
11	Octane	568.8	24.9	492.0	0.398	0.00
12	Decane	617.7	21.2	603.0	0.489	0.00
13	Propane	369.8	42.5	203.0	0.153	0.00
14	Isobutane	408.2	36.5	263.0	0.183	0.10
15	Propylene	364.9	46.0	181.0	0.144	0.40
16	R23	299.3	48.6	132.7	0.260	1.60
17	R32	351.6	58.3	120.8	0.271	2.00
18	R143a	346.3	37.6	194.0	0.251	2.30
19	R152a	386.7	45.0	181.0	0.256	2.30
20	R12	385.0	41.4	216.7	0.204	0.54
21	R22	369.3	49.7	165.6	0.221	1.40
22	R13	302.0	38.7	180.4	0.198	0.50
23	R142b	409.6	43.3	231.0	0.251	2.10
24	R115	353.2	32.3	251.8	0.279	0.34

Table 5.3 Optimized average absolute deviations of vapor phase composition $\left(\frac{\Delta Y_1}{y_1}\right)$ and pressure $\left(\frac{\Delta P}{P}\right)$ and Objective Function (OF)

SYSTEM	TEMP (K)	PRM1			PRM2			QM1			QM2		
		$\Delta Y/Y$	$\Delta P/P$	OF									
Methanol(1)-Ethanol(2)	298.15	0.0174	0.0249	0.0148	0.0124	0.0234	0.0112	0.0198	0.0333	0.0240	0.0208	0.0283	0.0198
Methanol(1)-Propanol(2)	333.17	0.0391	0.0624	0.1410	0.0342	0.0613	0.1280	0.0129	0.0318	0.0307	0.0090	0.209	0.0134
Methanol(1)-1-Butanol(2)	298.15	0.0752	0.1111	0.4140	0.0801	0.1045	0.3988	0.0392	0.0536	0.1016	0.0430	0.0496	0.0991
Ethanol(1)-1-Butanol(2)	323.15	0.1134	0.0985	0.1805	0.1071	0.1026	0.1761	0.0626	0.0590	0.0592	0.0515	0.0652	0.0553
	343.15	0.0706	0.0653	0.0740	0.0616	0.0655	0.0658	0.0304	0.0264	0.0130	0.0204	0.0305	0.0108
	363.15	0.0325	0.0372	0.0195	0.0275	0.0356	0.0162	0.0119	0.0139	0.0027	0.0132	0.0124	0.0026
	383.15	0.0222	0.0229	0.0081	0.0155	0.0175	0.0044	0.0185	0.0278	0.0089	0.0202	0.0248	0.0082
	403.15	0.0021	0.0150	0.0018	0.0047	0.0106	0.0011	0.0326	0.0494	0.0281	0.0342	0.0425	0.0238
Methanol(1)-Benzene(2)	308.15	0.2666	0.1353	0.8044	0.0876	0.0461	0.0882	0.2839	0.1631	0.9650	0.1949	0.1006	0.4329
	318.15	0.2624	0.1312	2.8396	0.0868	0.0478	0.3242	0.2854	0.1580	3.5112	0.1822	0.1003	1.4276
	328.15	0.2061	0.1439	0.5688	0.0460	0.0289	0.0266	0.2215	0.1710	0.7046	0.0986	0.1561	0.3070
Methanol(1)-Toluene(2)	318.15	0.1550	0.1909	0.6648	0.0424	0.0597	0.0950	0.1520	0.1980	0.6851	0.1234	0.1343	0.3658
Ethanol(1)-Benzene(2)	298.15	0.1637	0.0599	0.3947	0.0613	0.0262	0.0577	0.1322	0.0601	0.2743	0.1077	0.0328	0.1648
	318.15	0.1716	0.0717	0.4844	0.0563	0.0305	0.0573	0.1412	0.0681	0.3440	0.1044	0.0270	0.1628
	323.15	0.1756	0.0841	0.6065	0.0590	0.0244	0.0653	0.1562	0.0830	0.5007	0.1053	0.0248	0.1872
	328.22	0.1538	0.0699	0.2569	0.0489	0.0190	0.0248	0.1302	0.0669	0.1928	0.0959	0.0242	0.0881
Ethanol(1)-Cyclohexane(2)	273.15	0.1458	0.0898	0.3812	0.0279	0.0257	0.0187	0.0907	0.1095	0.2628	0.0854	0.1008	0.2268
	283.15	0.2093	0.0874	1.0803	0.0923	0.0409	0.2141	0.1969	0.0998	1.0227	0.1462	0.0566	0.5164
	293.15	0.2123	0.0889	1.1125	0.0814	0.0379	0.1693	0.1834	0.0982	0.9089	0.1466	0.0520	0.5078
	298.15	0.1750	0.0764	0.3284	0.0591	0.0246	0.0369	0.1445	0.0870	0.2561	0.1075	0.0436	0.1211

Table 5.3 Optimized average absolute deviations of vapor phase composition $\left(\frac{\Delta Y_i}{Y_i} \right)$ and pressure $\left(\frac{\Delta P}{P} \right)$ and Objective Function (OF)

(continued.)

SYSTEM	TEMP (K)	PRM1			PRM2			QMI1			QMI2		
		$\Delta Y/Y$	$\Delta P/P$	OF									
Ethanol(1)-Toluene(2)	303.15	0.2284	0.0927	1.2762	0.0892	0.0347	0.1925	0.1679	0.0973	0.7908	0.1572	0.0637	0.6044
	323.15	0.1265	0.0631	0.1399	0.0318	0.0217	0.0104	0.0830	0.0714	0.0838	0.0695	0.0382	0.0440
	308.15	0.1651	0.1399	0.5620	0.0479	0.0411	0.0478	0.1245	0.1124	0.3374	0.0990	0.0853	0.2051
	318.15	0.2157	0.1747	1.4639	0.0580	0.0455	0.1032	0.1631	0.1391	0.8726	0.1193	0.0992	0.4575
	328.15	0.1139	0.1046	0.2870	0.0265	0.0242	0.0155	0.0878	0.0780	0.1654	0.0637	0.0534	0.0829
	333.15	0.0653	0.0796	0.1378	0.0153	0.0179	0.0072	0.0555	0.0531	0.0768	0.0296	0.0277	0.0213
1-Propanol(1)-Benzene(2)	318.15	0.1969	0.0715	0.5706	0.0767	0.0559	0.1171	0.0951	0.0491	0.1489	0.0272	0.0885	0.1114
	328.15	0.1912	0.0973	0.9205	0.0872	0.0465	0.1952	0.1419	0.0625	0.4806	0.0213	0.1038	0.2243
	348.15	0.1177	0.0637	0.2330	0.0360	0.0117	0.0186	0.0776	0.0477	0.1079	0.0429	0.0099	0.0253
	323.01	0.2553	0.1185	1.3470	0.1180	0.0446	0.2707	0.1979	0.1033	0.8472	0.1829	0.0493	0.6102
	328.15	0.3201	0.0957	1.8974	0.1656	0.0567	0.5210	0.2677	0.0723	1.3069	0.2386	0.0362	0.9902
	338.15	0.1940	0.0921	0.6456	0.0941	0.0202	0.1297	0.1256	0.0626	0.2757	0.1106	0.0352	0.1886
1-Propano(1)-Cyclohexane(2)	298.15	0.2625	0.2453	0.9033	0.1903	0.2526	0.7002	0.0870	0.1327	0.1762	0.0550	0.1374	0.1533
	318.15	0.3048	0.1120	1.1596	0.1907	0.1153	0.5462	0.1426	0.0508	0.2521	0.1025	0.0715	0.1718
	298.15	0.3775	0.2087	2.9776	0.2850	0.1827	1.8333	0.2420	0.1334	1.2220	0.2428	0.1243	1.1906
	318.15	0.4092	0.1654	2.7274	0.3016	0.1161	1.4621	0.2647	0.1148	1.1653	0.2649	0.1144	1.1653
	323.15	0.3846	0.1171	2.2633	0.2380	0.0737	0.8690	0.2755	0.0925	1.1826	0.2773	0.0734	1.1522
	343.15	0.2753	0.1176	1.4339	0.1591	0.0252	0.4151	0.2027	0.0945	0.8001	0.1870	0.0485	0.5972
1-Butanol(1)-Toluene(2)	333.31	0.1710	0.1099	0.7025	0.1008	0.0765	0.2723	0.0715	0.0506	0.1305	0.0745	0.0419	0.1242
	343.40	0.1345	0.0889	0.4416	0.0843	0.0520	0.1668	0.0438	0.0368	0.0556	0.0440	0.0253	0.0439

Table 5.3 Optimized average absolute deviations of vapor phase composition $\left(\frac{\Delta y_i}{y_i} \right)$ and pressure $\left(\frac{\Delta P}{P} \right)$ and Objective Function (OF)

(continued.)

SYSTEM	TEMP (K)	PRM1			PRM2			OM1			OM2		
		$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF
Pentane(1)-Benzene(2)	353.44	0.1136	0.0751	0.3152	0.0577	0.0440	0.0894	0.0447	0.0295	0.0488	0.0384	0.0126	0.0278
	373.15	0.0591	0.0287	0.0475	0.0240	0.0158	0.0091	0.0528	0.0204	0.0352	0.0214	0.0242	0.0115
	308.15	0.0094	0.0167	0.0051	0.0100	0.0157	0.0048	0.0121	0.0225	0.0091	0.0131	0.0219	0.0091
	313.15	0.0096	0.0127	0.0040	0.0096	0.0125	0.0040	0.0159	0.0270	0.0157	0.0179	0.0253	0.0154
	318.15	0.0254	0.0367	0.0320	0.0237	0.0365	0.0304	0.0286	0.0417	0.0409	0.0305	0.0381	0.0305
	323.15	0.0346	0.0211	0.0246	0.0256	0.0192	0.0153	0.0429	0.0345	0.0455	0.0444	0.0321	0.0450
Pentane(1)-Decane(2)	317.70	0.0012	0.0373	0.0126	0.0013	0.0315	0.0089	0.0015	0.0335	0.0101	0.0034	0.0148	0.0021
	333.70	0.0051	0.0239	0.0072	0.0051	0.0223	0.0063	0.0059	0.0479	0.0093	0.0054	0.0161	0.0035
Benzene(1)-Hexane(2)	298.15	0.0205	0.0259	0.0337	0.0180	0.0224	0.0255	0.0503	0.0344	0.1152	0.0063	0.0125	0.0061
	333.15	0.0070	0.0048	0.0023	0.0069	0.0041	0.0020	0.0628	0.0314	0.1528	0.0118	0.0111	0.0082
	283.15	0.0354	0.0675	0.0582	0.0337	0.0594	0.0466	0.0288	0.0396	0.0240	0.0163	0.0247	0.0088
	298.15	0.0207	0.0375	0.0238	0.0202	0.0366	0.0227	0.0237	0.0260	0.0161	0.0089	0.0160	0.0043
	303.15	0.0170	0.0298	0.0200	0.0165	0.0275	0.0175	0.0234	0.0228	0.0181	0.0070	0.0126	0.0035
	313.15	0.0122	0.0206	0.0126	0.0121	0.0188	0.0110	0.0240	0.0211	0.0225	0.0074	0.0108	0.0038
Benzene(1)-Cyclohexane(2)	323.15	0.0092	0.0135	0.0091	0.0091	0.0125	0.0081	0.0267	0.0227	0.0417	0.0075	0.0095	0.0049
	333.15	0.0073	0.0090	0.0048	0.0066	0.0078	0.0038	0.0290	0.0224	0.0483	0.0065	0.0094	0.0047
	343.15	0.0052	0.0035	0.0005	0.0043	0.0035	0.0004	0.0248	0.0174	0.0129	0.0084	0.0092	0.0022
	403.15	0.0092	0.0106	0.0026	0.0092	0.0104	0.0025	0.0263	0.0180	0.0132	0.0056	0.0126	0.0025
	413.15	0.0099	0.0107	0.0028	0.0100	0.0103	0.0027	0.0246	0.0183	0.0123	0.0085	0.0127	0.0030
	423.15	0.0093	0.0095	0.0023	0.0094	0.0094	0.0023	0.0247	0.0194	0.0128	0.0080	0.0134	0.0031

Table 5.3 Optimized average absolute deviations of vapor phase composition $\left(\frac{\Delta y_i}{y_i} \right)$ and pressure $\left(\frac{\Delta P}{P} \right)$ and Objective Function (OF)

(continued.)

SYSTEM	TEMP (K)	PRM1			PRM2			OM1			OM2		
		$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF
Benzene(1)-Heptane(2)	293.15	0.0235	0.0393	0.0420	0.0198	0.0268	0.0222	0.0289	0.0364	0.0432	0.0073	0.0183	0.0077
	318.15	0.0142	0.0162	0.0065	0.0122	0.0136	0.0047	0.0345	0.0231	0.0242	0.0090	0.0065	0.0017
	328.15	0.0140	0.0143	0.0052	0.0100	0.0102	0.0027	0.0356	0.0275	0.0263	0.0092	0.0113	0.0028
	333.15	0.0086	0.0070	0.0020	0.0087	0.0069	0.0020	0.0252	0.0182	0.0154	0.0119	0.0136	0.0052
	353.15	0.0125	0.0149	0.0064	0.0137	0.0099	0.0049	0.0243	0.0150	0.0139	0.0135	0.0121	0.0056
	413.15	0.0189	0.0056	0.0031	0.0081	0.0081	0.0011	0.0609	0.0106	0.0306	0.0129	0.0146	0.0030
	313.15	0.0123	0.0239	0.0109	0.0119	0.0210	0.0087	0.0078	0.0114	0.0029	0.0051	0.0097	0.0018
Benzene(1)-Toluene(2)	334.15	0.0041	0.0067	0.0010	0.0031	0.0069	0.0009	0.0063	0.0078	0.0016	0.0032	0.0072	0.0010
Benzene(1)-Octane(2)	328.15	0.0055	0.0105	0.0038	0.0054	0.0103	0.0036	0.0218	0.0113	0.0163	0.0128	0.0123	0.0085
Cyclohexane(1)-Hexane(2)	338.15	0.0066	0.0082	0.0029	0.0062	0.0075	0.0025	0.0251	0.0107	0.0193	0.0135	0.0140	0.0098
Toluene(1)-Decane(2)	348.15	0.0036	0.0071	0.0008	0.0034	0.0067	0.0007	0.0241	0.0141	0.0093	0.0081	0.0110	0.0023
Toluene(1)-Heptane(2)	298.15	0.0156	0.0219	0.0224	0.0137	0.0196	0.0177	0.0245	0.0155	0.0261	0.0063	0.0058	0.0023
	308.15	0.0119	0.0145	0.0057	0.0102	0.0132	0.0045	0.0283	0.0172	0.0176	0.0060	0.0071	0.0014
	343.15	0.0161	0.0072	0.0019	0.0123	0.0052	0.0011	0.0263	0.0122	0.0050	0.0085	0.0065	0.0007
	373.5	0.0324	0.0384	0.0277	0.0276	0.0403	0.0262	0.0297	0.0291	0.0190	0.0222	0.0302	0.0155
	383.6	0.0216	0.0403	0.0188	0.0162	0.0285	0.0097	0.0273	0.0344	0.0173	0.0282	0.0334	0.0172
	303.15	0.0195	0.0214	0.0092	0.0166	0.0201	0.0075	0.0319	0.0205	0.0158	0.0136	0.0184	0.0058

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Table 5.3 Optimized average absolute deviations of vapor phase composition $\left(\frac{\Delta y_i}{y_i} \right)$ and pressure $\left(\frac{\Delta P}{P} \right)$ and Objective Function (OF)

(continued.)

SYSTEM	TEMP (K)	PRM1			PRM2			QM1			QM2		
		$\Delta Y/Y$	$\Delta P/P$	OF									
Toluene(1)-Octane(2)	328.15	0.0111	0.0084	0.0019	0.0101	0.0087	0.0018	0.0330	0.0087	0.0117	0.0097	0.0080	0.0016
	333.15	0.0088	0.0160	0.0063	0.0081	0.0138	0.0048	0.0229	0.0149	0.0142	0.0081	0.0095	0.0030
	258.00	0.0181	0.0235	0.0079	0.0157	0.0235	0.0072	0.0078	0.0309	0.0091	0.0090	0.0305	0.0091
	263.00	0.0200	0.0234	0.0085	0.0192	0.0231	0.0081	0.0094	0.0302	0.0090	0.0103	0.0298	0.0089
	268.00	0.0182	0.0217	0.0072	0.0155	0.0217	0.0064	0.0063	0.0283	0.0076	0.0079	0.0278	0.0075
	273.00	0.0171	0.0203	0.0063	0.0144	0.0202	0.0055	0.0062	0.0274	0.0071	0.0086	0.0264	0.0069
	278.00	0.0196	0.0201	0.0071	0.0157	0.0201	0.0059	0.0092	0.0270	0.0073	0.0108	0.0262	0.0072
	283.00	0.0226	0.0211	0.0086	0.0218	0.0212	0.0084	0.0097	0.0248	0.0064	0.0099	0.0247	0.0064
	251.00	0.0210	0.0181	0.0077	0.0171	0.0205	0.0071	0.0071	0.0178	0.0037	0.0050	0.0170	0.0031
	273.00	0.0303	0.0091	0.0100	0.0175	0.0174	0.0061	0.0193	0.0177	0.0068	0.0160	0.0158	0.0051
Propylene(1)-R115(2)	251.00	0.0140	0.0226	0.0056	0.0094	0.0212	0.0043	0.0204	0.0327	0.0119	0.0129	0.0263	0.0068
	275.00	0.0088	0.0080	0.0011	0.0089	0.0078	0.0011	0.0283	0.0334	0.0153	0.0083	0.0198	0.0037
	298.00	0.0197	0.0130	0.0050	0.0201	0.0120	0.0049	0.0387	0.0403	0.0281	0.0128	0.0180	0.0044
	258.0	0.0048	0.0047	0.0004	0.0047	0.0045	0.0003	0.0185	0.0171	0.0051	0.0152	0.0190	0.0047
Propylene(1)-R22(2)	263.00	0.0043	0.0048	0.0003	0.0038	0.0046	0.0003	0.0176	0.0178	0.0050	0.0149	0.0194	0.0048

Table 5.3 Optimized average absolute deviations of vapor phase composition $\left| \frac{\Delta Y_i}{Y_i} \right|$ and pressure $\left| \frac{\Delta P}{P} \right|$ and Objective Function (OF)

(continued.)

SYSTEM	TEMP (K)	PRM1			PRM2			OM1			OM2		
		$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF	$\Delta Y/Y$	$\Delta P/P$	OF
Propylene(1)-R142b(2)	268.00	0.0047	0.0046	0.0003	0.0036	0.0045	0.0003	0.0169	0.0185	0.0050	0.0148	0.0197	0.0049
	273.00	0.0079	0.0068	0.0008	0.0073	0.0072	0.0007	0.0211	0.0188	0.0056	0.0170	0.0210	0.0051
	278.00	0.0028	0.0055	0.0003	0.0028	0.0055	0.0003	0.0181	0.0204	0.0060	0.0167	0.0214	0.0059
	283.00	0.0087	0.0076	0.0011	0.0089	0.0072	0.0010	0.0228	0.0195	0.0072	0.0171	0.0225	0.0064
	268.00	0.0134	0.0202	0.0041	0.0073	0.0139	0.0017	0.0178	0.0375	0.0121	0.0165	0.0376	0.0118
	278.00	0.0141	0.0151	0.0030	0.0116	0.0140	0.0023	0.0072	0.0346	0.0087	0.0074	0.0345	0.0087
	288.00	0.0191	0.0208	0.0072	0.0191	0.0196	0.0067	0.0108	0.0312	0.0098	0.0112	0.0309	0.0098
Propylene(1)-R23(2)	298.00	0.0254	0.0292	0.0120	0.0250	0.0295	0.0120	0.0132	0.0306	0.0089	0.0129	0.0307	0.0089
	251.00	0.0127	0.0061	0.0018	0.0113	0.0054	0.0014	0.0183	0.0393	0.0102	0.0215	0.0241	0.0094
	265.00	0.0350	0.0122	0.0110	0.0289	0.0133	0.0081	0.0527	0.0373	0.0334	0.0174	0.0299	0.0096
	255.00	0.0154	0.0173	0.0048	0.0132	0.0147	0.0035	0.0413	0.0316	0.0066	0.0120	0.0226	0.0039
	265.00	0.0145	0.0163	0.0043	0.0134	0.0143	0.0034	0.0146	0.0229	0.0087	0.0120	0.0273	0.0059
	275.00	0.0109	0.0138	0.0028	0.0082	0.0107	0.0016	0.0141	0.0277	0.0056	0.0111	0.0216	0.0080
	285.00	0.0109	0.0144	0.0029	0.0121	0.0122	0.0026	0.0115	0.0221	0.0054	0.0126	0.0211	0.0053
R32(1)-R143a(2)	263.15	0.0100	0.0082	0.0017	0.0092	0.0087	0.0016	0.0125	0.0211	0.0270	0.0083	0.0180	0.0054
	273.15	0.0182	0.0104	0.0044	0.0128	0.0082	0.0023	0.0513	0.0417	0.0437	0.0142	0.0208	0.0064
	283.15	0.0210	0.0110	0.0056	0.0157	0.0084	0.0032	0.0526	0.0406	0.0441	0.0162	0.0201	0.0067
	293.15	0.0253	0.0221	0.0113	0.0210	0.0177	0.0076	0.0615	0.0465	0.0595	0.0150	0.0233	0.0076
	303.15	0.0183	0.0145	0.0055	0.0183	0.0118	0.0047	0.0563	0.0395	0.0523	0.0152	0.0181	0.0056
	313.15	0.0148	0.0130	0.0039	0.0120	0.0107	0.0026	0.0455	0.0461	0.0058	0.0154	0.0027	

Table 5.4. Optimum binary interaction parameters of the systems

No	SYSYEM	TEMP (K)	No. Of Data Points	Model 1	Model 2	Model 3	Model 4
				k_{ij}	k_{ij}	k_{ij}	k_{ij}
1	Methanol(1)-Ethanol(2)	298.15	16	-0.0009	0.0043	-0.0039	-0.0158
2	Methanol(1)-Propanol(2)	333.17	26	-0.0077	-0.0184	-0.0030	-0.0368
3	Methanol(1)-1-Butanol(2)	298.15	23	-0.0163	-0.0080	-0.0234	-0.0506
4	Ethanol(1)-1-Butanol(2)	323.15	8	-0.0071	-0.0165	-0.0007	-0.0027
5	Methanol(1)-Benzene(2)	343.15	8	-0.0017	-0.0163	-0.0080	0.0002
6	Methanol(1)-Toluene(2)	363.15	8	0.0003	-0.0103	0.0070	-0.0183
7	Ethanol(1)-Benzene(2)	383.15	8	0.0073	-0.0057	0.0154	0.0086
8	Ethanol(1)-Cyclohexane(2)	403.15	8	0.0065	-0.0001	0.0105	0.0101
9	Ethanol(1)-Toluene(2)	308.15	9	0.0974	0.0241	0.1652	0.0548
		318.15	33	0.1037	0.0242	0.1811	0.0572
		328.15	9	0.1138	0.0345	0.1763	0.0668
		318.15	11	0.0860	0.0085	0.1693	0.0442
		298.15	13	0.0766	0.0366	0.1182	0.0609
		318.15	14	0.0916	0.0447	0.1381	0.0731
		323.15	16	0.0996	0.0444	0.1437	0.0786
		328.22	9	0.0955	0.0461	0.1415	0.0752
		273.15	13	0.0493	0.0314	0.0849	0.0405
		283.15	21	0.0653	0.0340	0.1138	0.0556
		293.15	21	0.0744	0.0370	0.1291	0.0621
		298.15	9	0.0803	0.0455	0.1264	0.0658
		303.15	21	0.0810	0.0350	0.1432	0.0673
		323.15	7	0.0982	0.0478	0.1546	0.0782
		308.15	12	0.0899	0.0126	0.1430	0.0767
		318.15	19	0.1111	0.0109	0.1563	0.0887
		328.15	12	0.0903	0.0296	0.1451	0.0765
		333.15	13	0.0872	0.0426	0.1327	0.0727

Table 5.4. Optimum binary interaction parameters of the systems (continued.)

No	SYSTEM	TEMP (K)	No. Of Data Points	Model 1	Model 2	Model 3	Model 4
				k_{ij}	k_{ij}	k_{ij}	k_{ij}
10	1-Propanol(1)-Benzene(2)	318.15	13	0.0787	0.0393	0.1095	0.0599
		328.15	20	0.0799	0.0460	0.1215	0.0614
		348.15	13	0.0878	0.0497	0.1132	0.0673
11	1-Propanol(1)-Cyclohexane(2)	323.01	17	0.0897	0.0129	0.1446	0.0782
		328.15	17	0.0899	0.0360	0.1602	0.0737
		338.15	14	0.0895	0.0483	0.1430	0.0769
12	1-Butanol(1)-Benzene(2)	298.15	7	0.0687	0.0397	0.0944	0.0415
		318.15	11	0.0698	0.0251	0.0957	0.0439
		298.15	16	0.0722	0.0457	0.1081	0.0558
13	1-Butanol(1)-Cyclohexane(2)	318.15	14	0.0818	0.0460	0.1273	0.0632
		323.15	14	0.0850	0.0226	0.1281	0.0684
		343.15	16	0.0936	0.0458	0.1312	0.0737
14	1-Butanol(1)-Toluene(2)	333.31	17	0.0686	0.0260	0.0923	0.0542
		343.40	17	0.0718	0.0342	0.0911	0.0547
		353.44	17	0.0733	0.0338	0.0938	0.0566
15	Pentane(1)-Benzene(2)	373.15	11	0.0706	0.0469	0.0898	0.0563
		308.15	14	0.0183	0.0207	0.0171	0.0043
		313.15	16	0.0182	0.0171	0.0188	0.0038
		318.15	16	0.0178	0.0131	0.0199	0.0034
		323.15	15	0.0198	0.0069	0.0258	0.0044
16	Pentane(1)-Decane(2)	317.70	9	0.0057	0.0124	-0.0190	-0.0296
		333.70	12	0.0054	0.0083	-0.0005	0.0260
		298.15	31	0.0094	0.0042	0.0126	0.0003
17	Benzene(1)-Hexane(2)	333.15	31	0.0090	0.0080	0.0098	-0.0022
		283.15	10	0.0233	0.0110	0.0308	0.0182
18	Benzene(1)-Cyclohexane(2)	298.15	13	0.0184	0.0151	0.0211	0.0148

Table 5.4. Optimum binary interaction parameters of the systems (continued.)

No	SYSTEM	TEMP (K)	No. Of Data Points	Model 1	Model 2	Model 3	Model 4
				k_{ij}	k_{ji}	k_{ij}	k_{ji}
19	Benzene(1)-Heptane(2)	303.15	17	0.0212	0.0167	0.0242	0.0161
		313.15	22	0.0217	0.0186	0.0236	0.0159
		323.15	34	0.0232	0.0214	0.0244	0.0170
		333.15	36	0.0237	0.0216	0.0250	0.0165
		343.15	14	0.0214	0.0228	0.0207	0.0149
		403.15	13	0.0219	0.0231	0.0209	0.0122
		413.15	13	0.0216	0.0235	0.0202	0.0118
		423.15	13	0.0221	0.0223	0.0220	0.0118
		293.15	20	0.0052	-0.0074	0.0124	-0.0082
		318.15	14	0.0056	0.0007	0.0089	-0.0081
20	Benzene(1)-Toluene(2)	328.15	13	0.0077	0.0008	0.0117	-0.0077
		333.15	16	0.0006	0.0009	0.0005	-0.0126
		353.15	17	-0.0030	0.0028	-0.0048	-0.0151
		413.15	8	0.0071	0.0167	-0.0110	-0.0188
		313.15	15	-0.0038	-0.0085	-0.0011	-0.0017
		334.15	16	-0.0021	-0.0032	-0.0015	-0.0012
		328.15	27	-0.0059	-0.0067	-0.0040	-0.0258
		338.15	26	-0.0045	-0.0029	-0.0080	-0.0255
		348.15	12	-0.0028	-0.0040	-0.0004	-0.0250
		298.15	31	-0.0072	-0.0116	-0.0043	-0.0044
21	Benzene(1)-Octane(2)	308.15	16	-0.0068	-0.0098	-0.0046	-0.0049
		343.15	6	-0.0089	-0.0129	-0.0035	-0.0096
		373.50	11	-0.0123	-0.0182	-0.0092	-0.0405
		383.60	9	-0.0054	0.0151	-0.0152	-0.0355
22	Cyclohexane(1)-Hexane(2)	303.15	11	0.0028	-0.0012	0.0056	-0.0026
		328.15	10	0.0071	0.0058	0.0089	-0.0033
23	Toluene(1)-Decane(2)	383.60	9	-0.0054	0.0151	-0.0152	-0.0357
		303.15	11	0.0028	-0.0012	0.0056	-0.0076
24	Toluene(1)-Heptane(2)	328.15	10	0.0071	0.0058	0.0089	-0.0076
							0.0031

Table 5.4. Optimum binary interaction parameters of the systems (continued.)

No	SYSTEM	TEMP (K)	No. Of Data Points	k_{ij}	Model 1	k_{ji}	Model 2	k_{ij}	Model 3	k_{ji}	Model 4
25	Toluene(1)-Octane(2)	333.15	19	0.0001	-0.0037	0.0023	-0.0117	-0.0224	-0.0103		
26	Propylene(1)-R12(2)	258.00	9	0.0253	0.0191	0.0346	0.0119	0.0107	0.0123		
		263.00	9	0.0247	0.0199	0.0319	0.0113	0.0100	0.0116		
		268.00	9	0.0245	0.0175	0.0346	0.0107	0.0089	0.0112		
		273.00	9	0.0249	0.0178	0.0350	0.0108	0.0078	0.0117		
		278.00	9	0.0240	0.0147	0.0367	0.0101	0.0076	0.0107		
		283.00	9	0.0207	0.0164	0.0266	0.0076	0.0072	0.0077		
		251.00	10	0.0639	0.0675	0.0605	0.0382	0.0368	0.0396		
		273.00	10	0.0620	0.0746	0.0499	0.0364	0.0332	0.0402		
27	Propylene(1)-R13(2)	251.00	8	0.0760	0.0854	0.0715	0.0453	0.0333	0.0477		
28	Propylene(1)-R115(2)	275.00	8	0.0785	0.0793	0.0780	0.0432	0.0252	0.0504		
		298.00	9	0.0858	0.0825	0.0874	0.0493	0.0173	0.0583		
		258.00	8	0.0330	0.0339	0.0321	0.0144	0.0171	0.0134		
		263.00	8	0.0337	0.0355	0.0321	0.0145	0.0169	0.0136		
		268.00	8	0.0340	0.0366	0.0318	0.0143	0.0164	0.0136		
		273.00	7	0.0327	0.0310	0.0341	0.0132	0.0174	0.0119		
		278.00	8	0.0348	0.0353	0.0345	0.0141	0.0157	0.0135		
		283.00	8	0.0324	0.0338	0.0313	0.0121	0.0173	0.0103		
		268.00	7	0.0211	0.0330	-0.0021	0.0138	0.0211	0.0124		
		278.00	7	0.0240	0.0310	0.0125	0.0159	0.0154	0.0160		
		288.00	9	0.0264	0.0324	0.0216	0.0158	0.0121	0.0161		
		298.00	8	0.0263	0.0250	0.0273	0.0162	0.0178	0.0160		
30	Propylene(1)-R142b(2)	251.00	9	0.1195	0.1228	0.1166	0.1040	0.0881	0.0594		
		265.00	8	0.1151	0.1246	0.1022	0.0678	0.0801	0.0570		
		255.00	9	0.0815	0.0901	0.0729	0.0482	0.0420	0.0493		
31	Propylene(1)-R23(2)	265.00	9	0.0837	0.0911	0.0767	0.0490	0.0426	0.0502		
32	Propylene(1)-R152a(2)										

Table 5.4. Optimum binary interaction parameters of the systems (continued.)

No	SYSTEM	TEMP (K)	No. Of Data Points	Model 1		Model 2		Model 3		Model 4	
				k_{ij}	k_{ji}	k_{ij}	k_{ji}	k_{ij}	k_{ji}	k_{ij}	k_{ji}
33	R32(1)-R143a(2)	275.00	9	0.0842	0.0934	0.0757	0.0487	0.0444	0.0444	0.0495	0.0495
		285.00	9	0.0823	0.0871	0.0780	0.0468	0.0471	0.0471	0.0467	0.0467
		263.15	10	0.0085	0.0066	0.0099	-0.0037	-0.0296	-0.0296	0.0027	0.0027
		273.15	10	0.0171	0.0049	0.0261	0.0013	-0.0339	0.0108	0.0108	0.0108
		283.15	10	0.0173	0.0031	0.0280	0.0011	-0.037	0.0118	0.0118	0.0118
		293.15	10	0.0249	0.0059	0.0416	0.0043	-0.0415	0.0211	0.0211	0.0211
		303.15	10	0.0185	0.0090	0.0266	0.0012	-0.0396	0.0150	0.0150	0.0150
		313.15	10	0.0184	0.0045	0.0306	0.0016	-0.0374	0.0148	0.0148	0.0148

Table 5.5: VLE Data for Methanol (1) – Ethanol (2)
Temperature: 298.15 K

Experimental Data				Model 1			Model 2		
x _i	y _i	P (Kpa)							
0.0000	0.0000	7.8590	0.0000	8.1030	0.0000	8.1030	0.0000	8.1030	
0.0431	0.0860	8.2300	0.0866	8.4908	0.0839	8.4633	0.0839	8.4633	
0.1129	0.2112	8.8420	0.2101	9.1096	0.2078	9.0660	0.2078	9.0660	
0.2564	0.4230	10.1310	0.4151	10.3463	0.4196	10.3466	0.4196	10.3466	
0.3110	0.4903	10.6280	0.4800	10.8047	0.4868	10.8370	0.4868	10.8370	
0.3879	0.5752	11.3160	0.5621	11.4392	0.5708	11.5206	0.5708	11.5206	
0.4135	0.6011	11.5570	0.5874	11.6476	0.5963	11.7450	0.5963	11.7450	
0.4843	0.6678	12.2040	0.6525	12.2171	0.6613	12.3543	0.6613	12.3543	
0.5563	0.7288	12.8610	0.7127	12.7861	0.7201	12.9532	0.7201	12.9532	
0.5654	0.7360	12.9370	0.7200	12.8573	0.7271	13.0273	0.7271	13.0273	
0.6206	0.7782	13.4510	0.7622	13.2862	0.7675	13.4680	0.7675	13.4680	
0.6437	0.7989	13.6570	0.7791	13.4641	0.7835	13.6479	0.7835	13.6479	
0.7296	0.8528	14.4420	0.8385	14.1182	0.8396	14.2942	0.8396	14.2942	
0.8303	0.9131	15.3650	0.9023	14.8717	0.9002	15.0075	0.9002	15.0075	
0.9656	0.9836	16.6040	0.9810	15.8676	0.9792	15.9015	0.9792	15.9015	
1.0000	1.0000	16.9160	1.0000	16.1188	1.0000	16.1188	1.0000	16.1188	
$\Delta p/p$				0.0249				0.0234	
$\Delta y/y$				0.0174				0.0124	
Objective Function				0.0148				0.0112	

Table 5.5: VLE Data for Methanol (1) – Ethanol (2) (continued.)
Temperature: 298.15 K

x_i	Experimental Data			Model 3		Model 4	
	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)	
0.0000	0.0000	7.8590	0.0000	7.3988	0.0000	7.3988	
0.0431	0.0860	8.2300	0.0912	7.8071	0.0898	7.7976	
0.1129	0.2112	8.8420	0.2199	8.4654	0.2171	8.4521	
0.2564	0.4230	10.1310	0.4296	9.8061	0.4249	9.8256	
0.3110	0.4903	10.6280	0.4949	10.3110	0.4894	10.3548	
0.3879	0.5752	11.3160	0.5765	11.0167	0.5697	11.1020	
0.4135	0.6011	11.5570	0.6014	11.2501	0.5941	11.3506	
0.4843	0.6678	12.2040	0.6652	11.8914	0.6564	12.0352	
0.5563	0.7288	12.8610	0.7235	12.5373	0.7132	12.7233	
0.5654	0.7360	12.9370	0.7305	12.6185	0.7200	12.8094	
0.6206	0.7782	13.4510	0.7710	13.1086	0.7595	13.3264	
0.6437	0.7989	13.6570	0.7871	13.3125	0.7752	13.5397	
0.7296	0.8528	14.4420	0.8437	14.0654	0.8308	14.3119	
0.8303	0.9131	15.3650	0.9044	14.9379	0.8924	15.1630	
0.9656	0.9836	16.6040	0.9808	16.0981	0.9765	16.1708	
1.0000	1.0000	16.9160	1.0000	16.3920	1.0000	16.3920	
							0.0283
	$\Delta p/p$			0.0333			0.0208
	$\Delta y/y$		0.0198				0.0198
	Objective Function		0.0240				

Table 5.6: VLE Data for Ethanol (1) – Benzene (2)
Temperature: 298.15 K

Experimental Data			Model 1		Model 2	
X _i	Y _i	P (Kpa)	Y _i	P (Kpa)	Y _i	P (Kpa)
0.0000	0.0000	12.7700	0.0000	13.3849	0.0000	13.3849
0.0650	0.2310	16.1600	0.1352	14.5462	0.1927	15.6969
0.1870	0.2780	16.7300	0.2802	15.7629	0.2974	16.9645
0.2570	0.2920	16.8300	0.3290	16.0769	0.3133	17.0788
0.3260	0.3100	16.9300	0.3629	16.2145	0.3189	17.0924
0.4830	0.3350	16.5700	0.4076	16.1874	0.3256	17.0424
0.5450	0.3480	16.4800	0.4179	16.1182	0.3330	16.9347
0.6130	0.3650	16.0900	0.4273	16.0219	0.3482	16.6585
0.7340	0.4170	15.2400	0.4472	15.7095	0.4064	15.4393
0.7700	0.4450	14.7300	0.4570	15.5215	0.4359	14.8281
0.7950	0.4640	14.4400	0.4662	15.3383	0.4613	14.3256
0.9430	0.7100	10.5600	0.6443	11.9818	0.7574	10.0991
1.0000	1.0000	7.9700	1.0000	8.1030	1.0000	8.1030
				0.0599		0.0262
				0.0613		
				0.3947		0.0577
Objective Function						

Table 5.6: VLE Data for Ethanol (1) – Benzene (2) (continued.)
T  mperature: 298.15 K

x_i	Experimental Data			Model 3		Model 4	
	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)	
0.0000	0.0000	12.7700	0.0000	13.1082	0.0000	13.1082	
0.0650	0.2310	16.1600	0.1359	14.4220	0.1669	14.9507	
0.1870	0.2780	16.7300	0.2592	15.6423	0.2970	16.3878	
0.2570	0.2920	16.8300	0.2950	15.9508	0.3303	16.6017	
0.3260	0.3100	16.9300	0.3177	16.1197	0.3499	16.6073	
0.4830	0.3350	16.5700	0.3456	16.2928	0.3724	16.2997	
0.5450	0.3480	16.4800	0.3527	16.3208	0.3784	16.1236	
0.6130	0.3650	16.0900	0.3607	16.3111	0.3861	15.8912	
0.7340	0.4170	15.2400	0.3842	16.0024	0.4118	15.2223	
0.7700	0.4450	14.7300	0.3967	15.7536	0.4258	14.8898	
0.7950	0.4640	14.4400	0.4081	15.5063	0.4385	14.5968	
0.9430	0.7100	10.5600	0.6123	11.4416	0.6505	10.7763	
1.0000	1.0000	7.9700	1.0000	7.3988	1.0000	7.3988	
	$\Delta p/p$			0.0601		0.0328	
	$\Delta y/y$	0.1322		0.1077			
	Objective Function	0.2743		0.1648			

Table 5.7: VLE Data for Benzene (1) – Toluene (2)
Temperature: 334.15 K

Experimental Data				Model 1		Model 2	
x_i	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)	
0.0000	0.0000	19.2900	0.0000	19.6116	0.0000	19.6116	
0.0622	0.1535	21.5720	0.1520	21.7104	0.1527	21.7314	
0.1140	0.2589	23.3290	0.2583	23.4685	0.2589	23.4941	
0.1680	0.3516	25.1690	0.3538	25.3112	0.3539	25.3316	
0.2334	0.4519	27.5210	0.4528	27.5559	0.4522	27.5606	
0.3003	0.5390	29.9360	0.5390	29.8663	0.5379	29.8483	
0.3368	0.5802	31.2100	0.5807	31.1328	0.5794	31.1010	
0.4288	0.6683	34.3260	0.6726	34.3426	0.6711	34.2768	
0.4799	0.7128	36.2040	0.7167	36.1358	0.7153	36.0538	
0.5873	0.7949	39.9920	0.7967	39.9266	0.7957	39.8232	
0.6571	0.8372	42.3280	0.8411	42.4046	0.8405	42.2989	
0.7891	0.9091	46.9170	0.9122	47.1156	0.9124	47.0333	
0.8374	0.9332	48.5570	0.9348	48.8457	0.9351	48.7798	
0.8981	0.9574	50.6450	0.9610	51.0233	0.9613	50.9818	
0.9478	0.9810	52.3490	0.9807	52.8081	0.9810	52.7875	
1.0000	1.0000	54.0590	1.0000	54.6832	1.0000	54.6832	
		$\Delta p/p$		0.0067		0.0069	
		$\Delta y_i/y_i$		0.0041	0.0031		
		Objective Function		0.0010	0.0009		

Table 5.7: VLE Data for Benzene (1) – Toluene (2) (continued.)
Temperature: 334.15 K

X_1	Experimental Data			Model 3		Model 4	
	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)	
0.0000	0.0000	19.2900	0.0000	19.3405	0.0000	19.3405	
0.0622	0.1535	21.5720	0.1531	21.5297	0.1539	21.5416	
0.1140	0.2589	23.3290	0.2587	23.3492	0.2599	23.3581	
0.1680	0.3516	25.1690	0.3527	25.2434	0.3543	25.2382	
0.2334	0.4519	27.5210	0.4495	27.5358	0.4516	27.5006	
0.3003	0.5390	29.9360	0.5335	29.8807	0.5362	29.8035	
0.3368	0.5802	31.2100	0.5741	31.1609	0.5772	31.0574	
0.4288	0.6683	34.3260	0.6637	34.3935	0.6678	34.2186	
0.4799	0.7128	36.2040	0.7069	36.1946	0.7117	35.9803	
0.5873	0.7949	39.9920	0.7861	39.9999	0.7918	39.7162	
0.6571	0.8372	42.3280	0.8307	42.4925	0.8366	42.1819	
0.7891	0.9091	46.9170	0.9041	47.2646	0.9094	46.9688	
0.8374	0.9332	48.5570	0.9281	49.0347	0.9327	48.7728	
0.8981	0.9574	50.6450	0.9562	51.2816	0.9598	51.0887	
0.9478	0.9810	52.3490	0.9781	53.1420	0.9801	53.0305	
1.0000	1.0000	54.0590	1.0000	55.1188	1.0000	55.1188	
	$\Delta p/p$			0.0078		0.0072	
	$\Delta y/y$	0.0063		0.0032			
	Objective Function	0.0016		0.0010			

Table 5.8: VLE Data for Propylene (1) – R12 (2)
Temperature: 258.00 K

Experimental Data			Model 1		Model 2	
X _i	Y _i	P (Kpa)	Y _i	P (Kpa)	Y _i	P (Kpa)
0.0000	0.0000	181.3000	0.0000	169.96210	0.0000	169.9621
0.2391	0.4031	235.3000	0.4199	230.330	0.4206	233.0194
0.3524	0.5295	258.7000	0.5424	254.4664	0.5367	255.7733
0.4754	0.6357	280.0000	0.6494	278.1421	0.6407	277.7457
0.5745	0.7157	297.9000	0.7236	295.6404	0.7155	294.1629
0.7037	0.8143	320.0000	0.8108	316.7458	0.8064	314.5673
0.8283	0.8909	337.8000	0.8900	335.6165	0.8900	333.6757
0.9060	0.9406	349.0000	0.9391	346.7621	0.9406	345.4592
1.0000	1.0000	362.4000	1.0000	359.6500	1.0000	359.6556
$\Delta p/p$			0.0235		0.0235	
Objective Function			0.0181	0.0157	0.0079	0.0072

Table 5.8: VLE Data for Propylene (1) – R12 (2) (continued.)
Temperature: 258.00 K

x_i	Experimental Data			Model 3		Model 4	
	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)	
0.0000	0.0000	181.3000	0.0000	169.5218	0.0000	169.5218	
0.2391	0.4031	235.3000	0.4097	228.4935	0.4107	228.7176	
0.3524	0.5295	258.7000	0.5337	253.4825	0.5348	253.6015	
0.4754	0.6357	280.0000	0.6433	278.9858	0.6445	278.9108	
0.5745	0.7157	297.9000	0.7195	298.5516	0.7208	298.3044	
0.7037	0.8143	320.0000	0.8089	323.0537	0.8103	322.6322	
0.8283	0.8909	337.8000	0.8896	345.8831	0.8908	345.4399	
0.906	0.9406	349.0000	0.9391	359.8201	0.9400	359.4898	
1.0000	1.0000	362.4000	1.0000	376.4215	1.0000	376.4215	
	$\Delta p/p$			0.309		0.0305	
	$\Delta y/y$		0.0078		0.0090		
	Objective Function		0.0091		0.0091		

Table 5.9: VLE Data for Propylene (1) – R22 (2)
Temperature: 258.00 K

Experimental Data			Model 1		Model 2	
x_i	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)
0.0000	0.0000	294.9000	0.0000	292.1311	0.0000	292.1311
0.1517	0.2167	321.8000	0.2163	321.3227	0.2160	321.0368
0.3830	0.4460	348.7000	0.4473	348.9776	0.4483	348.9518
0.6070	0.6383	363.1000	0.6333	362.6578	0.6342	362.9412
0.6633	0.6831	364.9000	0.6797	364.4075	0.6803	364.743
0.7465	0.7562	366.9000	0.7503	365.7577	0.7505	366.1372
0.8133	0.8138	367.0000	0.8099	365.7269	0.8097	366.1013
1.0000	1.0000	362.4000	1.0000	359.6556	1.0000	359.6556
$\Delta p/p$			0.0047		0.0045	
$\Delta y/y$			0.0048		0.0047	
Objective Function			0.0004		0.0003	

Table 5.9: VLE Data for Propylene (1) – R22 (2) (continued.)
 Temperature: 258.00 K

x_i	Experimental Data			Model 3		Model 4	
	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)	
0.0000	0.0000	294.9000	0.0000	296.8195	0.0000	296.8195	
0.1517	0.2167	321.8000	0.2144	322.6601	0.2125	322.1326	
0.3830	0.4460	348.7000	0.4571	349.6779	0.4543	349.9442	
0.6070	0.6383	363.1000	0.6533	365.9699	0.6495	367.4128	
0.6633	0.6831	364.9000	0.7009	368.8374	0.6968	370.4716	
0.7465	0.7562	366.9000	0.7715	372.239	0.7674	373.9865	
0.8133	0.8138	367.0000	0.8291	374.2551	0.8253	375.8985	
1.0000	1.0000	362.4000	1.0000	376.4215	1.0000	376.4215	
	$\Delta p/p$			0.0171		0.0190	
	$\Delta y/y$		0.0185		0.0152		
	Objective Function		0.0051		0.0047		

Table 5.10: VLE Data for Propylene (1) – R152a (2)
Temperature: 255.00 K

Experimental Data			Model 1		Model 2	
X _i	Y _i	P (Kpa)	Y _i	P (Kpa)	Y _i	P (Kpa)
0.0000	0.0000	130.5000	0.0000	135.5887	0.0000	135.5887
0.1503	0.4378	205.4000	0.4290	210.4066	0.4236	207.2523
0.2947	0.5875	249.9000	0.5792	253.8350	0.5847	253.4496
0.4237	0.6778	279.1000	0.6584	279.2260	0.6680	281.2767
0.5610	0.7392	300.1000	0.7238	298.3785	0.7326	301.6835
0.6857	0.7927	313.7000	0.7810	311.4084	0.7858	314.8506
0.8220	0.8608	324.9000	0.8544	321.6038	0.8531	324.5777
0.8994	0.9100	328.7000	0.9076	324.9017	0.9040	327.2146
1.0000	1.0000	326.1000	1.0000	324.7041	1.0000	324.7041
		$\Delta p/p$		0.0173		0.0147
		$\Delta y/y$	0.0154		0.0132	
		Objective Function	0.0048		0.0035	

Table 5.10: VLE Data for Propylene (1) – R152a (2) (continued.)
Temperature: 255.00 K

x_1	Experimental Data			Model 3		Model 4	
	y_1	P (Kpa)	y_1	P (Kpa)	y_1	P (Kpa)	
0.0000	0.0000	130.5000	0.0000	136.2119	0.0000	136.2119	
0.1503	0.4378	205.4000	0.4255	209.4770	0.4294	210.4890	
0.2947	0.5875	249.9000	0.5779	252.6229	0.5823	253.1433	
0.4237	0.6778	279.1000	0.6609	279.0476	0.6662	278.5583	
0.5610	0.7392	300.1000	0.731	300.2329	0.7377	298.5035	
0.6857	0.7927	313.7000	0.7921	315.6532	0.7998	313.0185	
0.8220	0.8608	324.9000	0.8669	329.1499	0.8743	326.3396	
0.8994	0.9100	328.7000	0.9179	334.9652	0.9236	332.7852	
1.0000	1.0000	326.1000	1.0000	339.5474	1.0000	339.5474	
				0.0316		0.0226	
			0.0413		0.0120		
	Objective Function		0.0066		0.0039		

Table 5.11: VLE Data for R32 (1) – R143a (2)
Temperature: 263.15 K

x_i	Experimental Data			Model 1		Model 2	
	y_i	P (Kpa)	y_i	P (Kpa)	y_i	P (Kpa)	
0.0000	0.0000	450.1000	0.0000	450.2438	0.0000	450.2438	
0.0996	0.1384	475.4000	0.1400	475.2265	0.1405	475.6780	
0.1842	0.2448	497.0000	0.2453	494.7715	0.2453	495.2426	
0.2938	0.3663	524.1000	0.3672	517.7120	0.3663	517.8904	
0.4189	0.4798	545.5000	0.4909	540.4769	0.4892	540.1082	
0.5664	0.6112	565.1000	0.6221	562.3887	0.6204	561.3766	
0.6564	0.6984	577.7000	0.6975	572.9733	0.6964	571.6846	
0.7908	0.8076	589.6000	0.8086	584.4259	0.8088	583.0386	
0.8846	0.889	585.0000	0.8893	588.8094	0.8901	587.7076	
1.0000	1.0000	580.4000	1.0000	588.7885	1.0000	588.7885	
				0.0082		0.0087	
	$\Delta p/p$						
	$\Delta y/y$	0.0100		0.0092			
	Objective Function	0.0017		0.0016			

Table 5.11: VLE Data for R32 (1) – R143a (2) (continued)
Temperature: 263.15 K

Experimental Data				Model 3		Model 4	
X _i	y _i	P (Kpa)	y _i	P (Kpa)	y _i	P (Kpa)	
0.0000	0.0000	450.1000	0.0000	453.5821	0.0000	453.5821	
0.0996	0.1384	475.4000	0.1328	481.459	0.1398	484.3068	
0.1842	0.2448	497.0000	0.2321	503.6601	0.2424	505.8483	
0.2938	0.3663	524.1000	0.3464	530.3074	0.3600	528.1092	
0.4189	0.4798	545.5000	0.4621	557.6076	0.4802	546.9488	
0.5664	0.6112	565.1000	0.5857	584.9856	0.6112	562.6781	
0.6564	0.6984	577.7000	0.6581	598.6091	0.6889	570.3072	
0.7908	0.8076	589.6000	0.7699	612.8996	0.8061	581.3645	
0.8846	0.889	585.0000	0.8585	616.2197	0.8909	590.5637	
1.0000	1.0000	580.4000	1.0000	606.1500	1.0000	606.1500	
$\Delta p/p$				0.0211		0.0180	
$\Delta y/y$				0.0125	0.0083		
Objective Function				0.0270	0.0054		

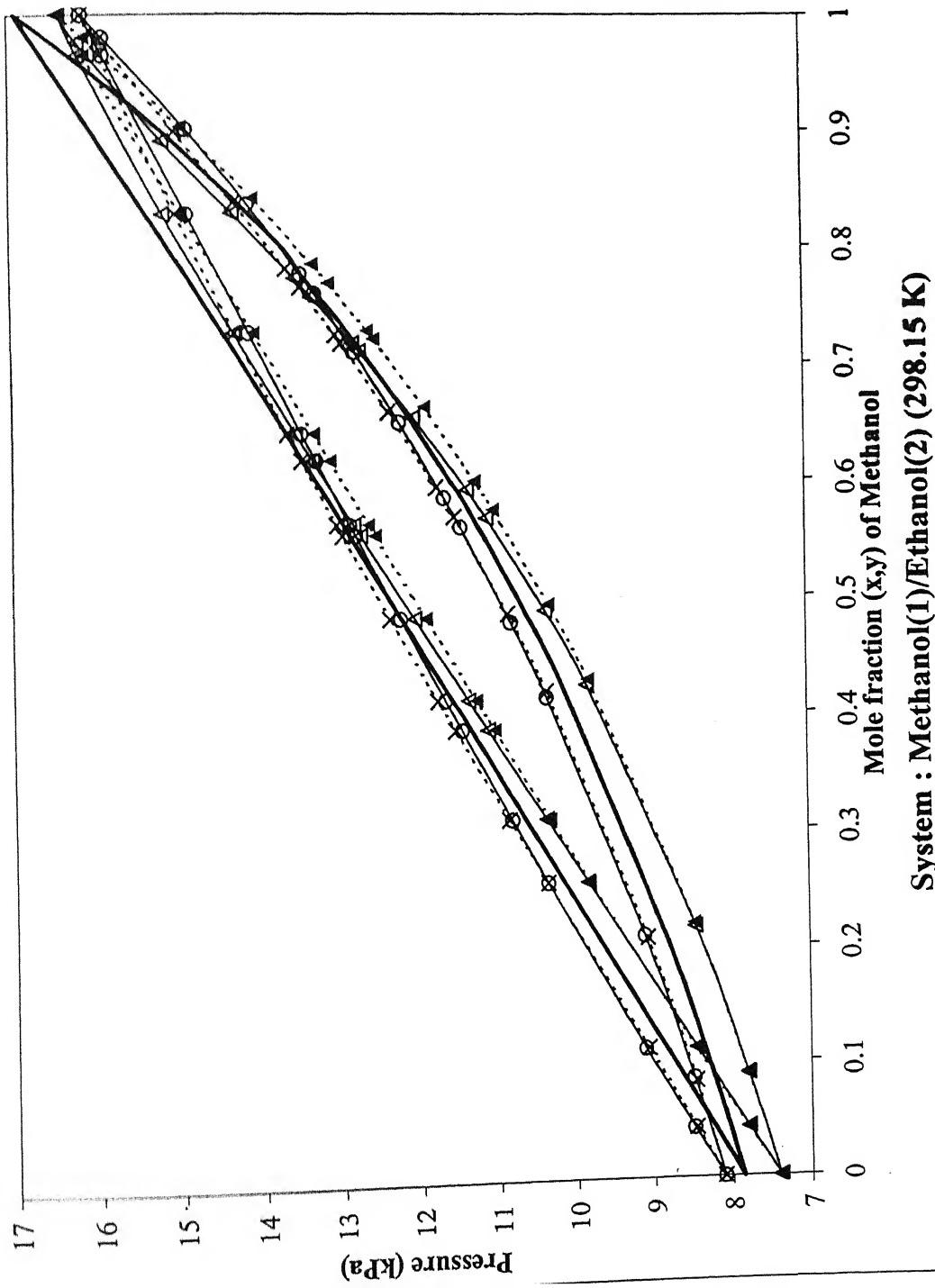


Figure 5.1 P - x - y diagram for Methanol (1)/Ethanol (2) system at 298.15 K

CHAPTER 6

CONCLUSIONS

Based on the present study it is evident that the VLE data predicted by the PR EOS with composition dependent mixing rule of Margules type with two binary interaction parameters is in good agreement with the experimentally obtained VLE data. This conclusion is valid for most of the systems, especially the nonpolar systems and refrigerant mixtures.

The Quartic EOS is expected to predict the VLE data better in view of the presence of dipole moment parameter and its complexity when compared to PR EOS. But this appears to be true only for highly non polar mixtures only. From the present study it can be concluded that the two binary interaction parameter mixing rules predicts the VLE data much better than vdW single binary interaction parameter mixing rule. This is true for both PR EOS and Quartic EOS.

Further studies can be carried out for the prediction of VLE data of a large number of systems using both these EOS to judge which one is superior. As a continuation of the work presented, it is also suggested that two parameter mixing rules viz. the Van Laar type, be used.

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Appendix A

A1 Program Code for VLE data by Model I

% Matlab commands contained in the file “Model1.m”.

```
function Model1(); %Main function i.e. calls other functions to calculate optimum  
min=fmin('pr',-0.1,0.23) %binary interaction parameters and VLE data corresponding to  
%that values.  
%”min” is the vector containing the final interaction parameters  
%where the objective function becomes minimum. ”pr” is the  
%function for VLE.”fmin” subfunction minimizing a function  
%one variable using golden section search algorithm and the two  
%values are the boundaries in which one tries to find the  
%minima.
```

%Control is passed onto the file “pr.m”. “pr.m” contains the following commands.

```
Function OF=pr(kij) %OF is the objective function value which is passed to the  
global I; %“fmin” function and “kij” is the value passed by “fmin”.  
I=2; %Initialization of the required data.  
j=1;STATEL=0;STATEV=1;  
n=8; %Benzene&Heptane  
Xexpt=[0.0000,0.3516,0.5252,0.5633,0.6083,0.6513,0.6731,1.0000]; % Vector with experimental  
Yexpt=[0.0000,0.4748,0.6479,0.6671,0.7192,0.7351,0.7536,1.0000]; %Vector with experimental  
Pexpt=[298.5,384.2,418.6,425.0,430.9,436.0,440.6,473.2]; %experimental 'P'  
T=413.15; % temperature  
Tc=[562.2,540.3]; %Critical temperature of components 1 and 2.  
Pc=[48.9,27.4]; %Critical pressure of components 1 and 2.  
vc=[0.259,0.432]; %Critical volumes of components 1 and 2.  
w=[0.212,0.349]; % Acentric factors of components 1 and 2  
  
for j=1:n % Loop changing experimental ‘x’ values  
    x(1)=Xexpt(j);  
    x(2)=(1-x(1));  
    P=0;  
    psat(2)=Pexpt(1);  
    psat(1)=Pexpt(n);  
    P=x(1)*psat(1)+x(2)*psat(2); %Initial guess of total pressure  
    sumy1=0;  
    P1=0;  
  
    while(sumy1~=1)
```

```

if(abs(P-P1)<1e-05)
    break;
end
for i=1:I
    k(i)=psat(i)/P;
    y(i)=k(i)*x(i);
end
t=1;
[phi]= pi1(T,P,x,Tc,Pc,w,STATEL,kij); %Control passes to "pi1.m" where fugacity coefficient
%for liquid phase is calculated. The code for "pi1.m" is
% given at the bottom.

phil=phi;
cond1=1;cond2=1;
while(1)
    if((cond1==0)&(cond2==0))
        break;
    end
t=1;
[phi]=pi1(T,P,y,Tc,Pc,w,STATEV,kij); % Fugacity coefficient for the vapor phase is
% calculated using "pi1.m"

phiv=phi;
sumy1=0;
for i=1:I
    y1(i)=(phil(i)*x(i))/phiv(i); % y' is calculated from fugacity coefficients.
    sumy1=sumy1+y1(i);
end
for i=1:I
    if(i==1)
        if(abs(y(i)-y1(i))<1.0e-06)
            cond1=0;
        end
    end
    if(i==2)
        if(abs(y(i)-y1(i))<1.0e-06)
            cond2=0;
        end
    end
    y(i)=y1(i);
end
end
P1=P;
P=P*sumy1;
end
Ycal(j)=y(1);
Pthe(j)=P;
end
OF=0;OFY=0;OFP=0;

```

% Check if old and new values for 'y' are within
% tolerable limit for component 1.

% Check if old and new values for 'y' are within
% tolerable limit for component 2.

%Change the value of 'y' to new.

% end of inner "while" loop

%New guess value for pressure

% end of outer "while" loop

%Put calculated values of 'y' into vector.

%Put calculated values of pressure into vector.

% end of outer "for"loop

```

if((Ycal(1)==0)&(Yexpt(1)==0))
    OFY=0;
else
    OFY=OFY+(((Yexpt(1)-Ycal(1))/Yexpt(1))^2);
end
for i=2:n
    OFY=OFY+(((Yexpt(i)-Ycal(i))/Yexpt(i))^2); %Objective function of %composition.
end
for i=1:n
    OFP=OFP+(((Pexpt(i)-Pthe(i))/Pexpt(i))^2); %Objective function of pressure.
end
OF=OFY+OFP %Overall objective function.

```

%Code for function “pi1.m” is given below.

```

function [phi]=pi1(T,P,x,Tc,Pc,w,state,ki) %calculates fugacity coefficient.
R = 8.314;
for i=1:2
    s(i)=0.37464+(1.54226*w(i))-(0.26992*(w(i)^2)); %
    alpha(i)=((1+s(i)*(1-sqrt(T/Tc(i))))^2); % PR EOS parameters.
    ai(i)=0.45724*((R*Tc(i))^2)*alpha(i)/(Pc(i)*100000); %
    bi(i)=(0.07780*R*Tc(i))/(Pc(i)*100000); %
end
a=amix(x,ai,ki); % EOS parameter ‘a’ for mixture
b=bmix(x,bi); %EOS parameter ‘b’ for mixture
A=(a*P*1000)/((R*T)^2);
B=(b*P*1000)/(R*T);
p=(B-1); %-(1-B)
q=(A-(3.0*(B^2))-(2.0*B)); % coefficients of the cubic equation of compressibility factor.
r=((B^3)+(B^2)-(A*B)); %
ro=[1 p q r]; %
Z=roots(ro); % Roots (Compressibility factor) are found out.
Big=0;Small=0;
if(state==1) %
if((imag(Z(1))==0)&(real(Z(1))>=0)) %
    Big=real(Z(1));
end %
if((imag(Z(2))==0)&(real(Z(2))>=0)) %
    if((real(Z(2)))>(real(Z(1)))) %
        Big=real(Z(2));
    end %
end %
if((imag(Z(3))==0)&(real(Z(3))>=0)) %
    if(Big<(real(Z(3)))) %
        Big=(real(Z(3)));
    end %
end %
Z1=Big; %

```

```

end %  

%  

if(state==0) %  

    if((imag(Z(1))==0)&(real(Z(1))>=0)) %  

        Small=real(Z(1)); %  

    End %  

    if((imag(Z(2))==0)&(real(Z(2))>=0)) %  

        if((real(Z(2)))<(real(Z(1)))) %  

            Small=real(Z(2)); %  

        end %  

    end %  

    if((imag(Z(3))==0)&(real(Z(3))>=0)) %  

        if(Small>(real(Z(3)))) %  

            Small=(real(Z(3))); %  

        elseif(Small==0) %  

            Small=real(Z(3)); %  

        end %  

    end %  

end %  

Z1=Small; %  

end %  

a12=(x(1)*ai(1)+(x(2)*(sqrt(ai(1)*ai(2)))*(1.0-ki)));  

a21=(x(2)*ai(2)+(x(1)*(sqrt(ai(1)*ai(2)))*(1.0-ki)));  

phi(1)=exp(((bi(1)/b)*(Z1-1)-(log(Z1-B))+((a/(2*sqrt(2)*b*R*T))*((bi(1)/b)-((2*a12/a)))*(log((Z1+B*(1+sqrt(2.0)))/(Z1+B*(1-sqrt(2.0))))))); % Fugacity coefficients % of both the  

phi(2)=exp(((bi(2)/b)*(Z1-1)-(log(Z1-B))+((a/(2*sqrt(2)*b*R*T))*((bi(2)/b)-((2*a21/a)))*(log((Z1+B*(1+sqrt(2.0)))/(Z1+B*(1-sqrt(2.0))))))); % components. %

```

% Code for calculating mixture parameters ‘a’ and ‘b’ “amix.m” and “bmix.m”

```

function a = amix(x,ai,ki)  

a =((x(1)^2)*ai(1)+(x(2)^2)*ai(2)+2.0*x(1)*x(2)*sqrt(ai(1)*ai(2))*(1.0-ki));  

function b=bmix(x,bi)  

b=x(1)*bi(1)+x(2)*bi(2);

```

A2 Program Code for VLE data by Model II

% Matlab commands contained in the file “Model2.m”.

```

function Model2(); %Main function i.e. calls other functions to calculate optimum

```

%binary interaction parameters and VLE data corresponding to
%that values.

kij=[0, 0]

min=fmins('prsv',kij) % "min" is the vector containing the final interaction parameters
% where the objective function becomes minimum. "prsv" is the
%function for VLE."fmin" subfunction minimizing a function
%one variable using golden section search algorithm and the two
%values are the boundaries in which one tries to find the
% minima.

%Control is passed onto the file “prsv.m”. “prsv.m” contains the following commands.

```
function OF=prsv(kij)          %OF is the objective function value which is passed to the
                                %“fmin” function and “kij” is the value passed by “fmin”.
global I;
I=2;                           %Initialization of the required data.
j=1;STATEL=0;STATEV=1;
n=8; %Benzene&Heptane
Xexpt=[0.0000,0.3516,0.5252,0.5633,0.6083,0.6513,0.6731,1.0000]; % Vector with experimental 'x'
Yexpt=[0.0000,0.4748,0.6479,0.6671,0.7192,0.7351,0.7536,1.0000]; %Vector with experimental 'y'
Pexpt=[298.5,384.2,418.6,425.0,430.9,436.0,440.6,473.2];           %experimental 'P'
T=413.15;                      % temperature
Tc=[562.2,540.3];              %Critical temperature of components 1 and 2.
Pc=[48.9,27.4];                %Critical pressure of components 1 and 2.
vc=[0.259,0.432];              %Critical volumes of components 1 and 2.
w=[0.212,0.349];               % Acentric factors of components 1 and 2

for j=1:n                         % Loop changing experimental 'x' values
    x(1)=Xexpt(j);
    x(2)=(1-x(1));
    P=0;
    psat(2)=Pexpt(1);
    psat(1)=Pexpt(n);
    P=x(1)*psat(1)+x(2)*psat(2);      %Initial guess of total pressure
    sumy1=0;
    P1=0;

    while(sumy1~=1)
        if(abs(P-P1)<1e-05)
            break;
        end
        for i=1:I
            k(i)=psat(i)/P;
            y(i)=k(i)*x(i);             %Initial guess for vapor composition 'y'.
        end
    t=1;
```

```

[phi]=prsvpi1(T,P,x,Tc,Pc,w,STATEL,kij);%Control passes to "prsvpi1.m" where fugacity
                                              %coefficient for liquid phase is calculated. The code for
                                              %"prsvpi1.m" is given at the bottom.

phil=phi;
cond1=1;cond2=1;
while(1)
    if((cond1==0)&(cond2==0))
        break;
    end
t=1;
[phi]=prsvpi1(T,P,y,Tc,Pc,w,STATEV,kij); % Fugacity coefficient for the vapor phase is
                                              % calculated using "prsvpi1.m"

phiv=phi;
sumy1=0;
for i=1:I
    y1(i)=(phil(i)*x(i))/phiv(i);           % y' is calculated from fugacity coefficients.
    sumy1=sumy1+y1(i);
end
for i=1:I
    if(i==1)
        if(abs(y(i)-y1(i))<1.0e-06)          % Check if old and new values for 'y' are within
            cond1=0;                           % tolerable limit for component 1.
        end
    end
    if(i==2)
        if(abs(y(i)-y1(i))<1.0e-06)          % Check if old and new values for 'y' are within
            cond2=0;                           % tolerable limit for component 2.
        end
    end
    y(i)=y1(i);                            %Change the value of 'y' to new.
end
end                                     % end of inner "while" loop

P1=P;
P=P*sumy1;                             %New guess value for pressure
end                                     % end of outer "while" loop
Ycal(j)=y(1);                          %Put calculated values of 'y' into vector.
Pthe(j)=P;                            %Put calculated values of pressure into vector.
end                                     % end of outer "for"loop

OF=0;OFY=0;OFP=0;
if((Ycal(1)==0)&(Yexpt(1)==0))
    OFY=0;
else
    OFY=OFY+(((Yexpt(1)-Ycal(1))/Yexpt(1))^2);
end
for i=2:n
    OFY=OFY+(((Yexpt(i)-Ycal(i))/Yexpt(i))^2); %Objective function of %composition.
end

```

```

for i=1:n
    OFP=OFP+(((Pexpt(i)-Pthe(i))/Pexpt(i))^2); %Objective function of pressure.
end
OF=OFY+OFP %Overall objective function.

```

%Code for function “prsvpil.m” is given below.

```

function [phi]=pi1(T,P,x,Tc,Pc,w,state,ki) %calculates fugacity coefficient.
R = 8.314;
for i=1:2
    s(i)=0.37464+(1.54226*w(i))-(0.26992*(w(i)^2)); %
    alpha(i)=((1+s(i)*(1-sqrt(T/Tc(i))))^2); % PR EOS parameters.
    ai(i)=0.45724*((R*Tc(i))^2)*alpha(i)/(Pc(i)*100000); %
    bi(i)=(0.07780*R*Tc(i))/(Pc(i)*100000); %
end
a=amix(x,ai,ki); % EOS parameter ‘a’ for mixture
b=bmix(x,bi); %EOS parameter ‘b’ for mixture
A=(a*P*1000)/((R*T)^2);
B=(b*P*1000)/(R*T);
p=(B-1); %-(1-B)
q=(A-(3.0*(B^2))-(2.0*B)); % coefficients of the cubic equation of compressibility factor.
r=((B^3)+(B^2)-(A*B)); %
ro=[1 p q r]; %
Z=roots(ro); % Roots (Compressibility factor) are found out.
Big=0;Small=0;
if(state==1) %
    if((imag(Z(1))==0)&(real(Z(1))>=0)) %
        Big=real(Z(1));
    end %
    if((imag(Z(2))==0)&(real(Z(2))>=0)) %Arrange the compressibility factors
        if((real(Z(2)))>(real(Z(1)))) %as vapor and liquid phase
            Big=real(Z(2));
        end %
    end %
    if((imag(Z(3))==0)&(real(Z(3))>=0)) % compressibility factors
        if(Big<(real(Z(3)))) %
            Big=(real(Z(3)));
        end %
    end %
    Z1=Big;
end %
if(state==0) %
    if((imag(Z(1))==0)&(real(Z(1))>=0)) %
        Small=real(Z(1));
    End %
    if((imag(Z(2))==0)&(real(Z(2))>=0)) %
        if((real(Z(2)))<(real(Z(1)))) %

```

```

Small=real(Z(2));
%
end
%
end
if((imag(Z(3))==0)&(real(Z(3))>=0))
%
if(Small>(real(Z(3))))
%
Small=(real(Z(3)));
%
elseif(Small==0)
%
Small=real(Z(3));
%
end
%
end
%
Z1=Small;
%
end
%
a12=(x(1)*ai(1)+x(2)*sqrt(ai(1)*ai(2))*(1.0-ki(1)*x(1)-
    ki(2)*x(2))+x(1)*(x(2)^2)*sqrt(ai(1)*ai(2))*(ki(2)-ki(1)));
%
a21=(x(2)*ai(2)+x(1)*sqrt(ai(1)*ai(2))*(1.0-ki(1)*x(1)-
    ki(2)*x(2))+x(2)*(x(1)^2)*sqrt(ai(1)*ai(2))*(ki(1)-ki(2)));
%
phi(1)=exp(((bi(1)/b)*(Z1-1))-(log(Z1-B)+(a/(2*sqrt(2)*b*R*T))*((bi(1)/b)-
    (2*a12/a))*(log((Z1+B*(1+sqrt(2.0)))/(Z1+B*(1-sqrt(2.0))))));
%
phi(2)=exp(((bi(2)/b)*(Z1-1))-(log(Z1-B)+(a/(2*sqrt(2)*b*R*T))*((bi(2)/b)-
    (2*a21/a))*(log((Z1+B*(1+sqrt(2.0)))/(Z1+B*(1-sqrt(2.0))))));
%
% Code for calculating mixture parameters 'a' and 'b' "prsvamix.m" and "prsvbmix.m"
%
function a = prsvamix(x,ai,ki)
a = ((x(1)^2)*ai(1)+((x(2)^2)*ai(2))+(2.0*x(1)*x(2)*sqrt(ai(1)*ai(2))*(
    1.0- ki(1)*x(1)-ki(2)*x(2))) ;
%
function b=prsvbmix(x,bi)
b=x(1)*bi(1)+x(2)*bi(2);

```

A3 Program Code for VLE data by Model III

% Matlab commands contained in the file "Modelq1.m".

```

function Modelq1(); %Main function i.e. calls other functions to calculate optimum
                    %binary interaction parameters and VLE data corresponding to
                    %that values.
min=fmin('qpr',-0.1,0.23) %"min" is the vector containing the final interaction parameters
                            %where the objective function becomes minimum. "qpr" is the
                            %function for VLE."fmin" subfunction minimizing a function

```

%one variable using golden section search algorithm and the two
 %values are the boundaries in which one tries to find the
 % minima.

%Control is passed onto the file “qpr.m”. “qpr.m” contains the following commands.

```

Function OF=qpr(kij)           %OF is the objective function value which is passed to the
                                %“fmin” function and “kij” is the value passed by “fmin”.
global I;
I=2;                          %Initialization of the required data.
j=1;STATEL=0;STATEV=1;
n=8; %Benzene&Heptane
Xexpt=[0.0000,0.3516,0.5252,0.5633,0.6083,0.6513,0.6731,1.0000]; % Vector with experimental 'x'
Yexpt=[0.0000,0.4748,0.6479,0.6671,0.7192,0.7351,0.7536,1.0000]; %Vector with experimental 'y'
Pexpt=[298.5,384.2,418.6,425.0,430.9,436.0,440.6,473.2];          %experimental 'P'
T=413.15;                     % temperature
Tc=[562.2,540.3];            %Critical temperature of components 1 and 2.
Pc=[48.9,27.4];              %Critical pressure of components 1 and 2.
vc=[0.259,0.432];             %Critical volumes of components 1 and 2.
mu=[0.0,0.0];                 %Dipole moment of components 1 and 2

for j=1:n                      % Loop changing experimental 'x' values
    x(1)=Xexpt(j);
    x(2)=(1-x(1));
    P=0;
    psat(2)=Pexpt(1);
    psat(1)=Pexpt(n);
    P=x(1)*psat(1)+x(2)*psat(2);      %Initial guess of total pressure
    sumy1=0;
    P1=0;

    'while(sumy1~=1)
        if(abs(P-P1)<1e-05)
            break;
        end
        for i=1:I
            k(i)=psat(i)/P;
            y(i)=k(i)*x(i);          %Initial guess for vapor composition 'y'.
        end
        t=1;
        [phi]= qpi1(T,P,x,Tc,Pc,mu,STATEL,kij);%Control passes to “qpi1.m” where fugacity coefficient
                                                %for liquid phase is calculated. The code for “qpi1.m”
                                                % given at the bottom.

    phil=phi;
    cond1=1;cond2=1;
    while(1)
        if((cond1==0)&(cond2==0))

```

```

break;
end
t=1;
[phi]=qpi1(T,P,y,Tc,Pc,mu,STATEV,kij); % Fugacity coefficient for the vapor phase is
% calculated using "qpi1.m"
phiv=phi;
sumy1=0;
for i=1:I
    y1(i)=(phil(i)*x(i))/phiv(i);           % y' is calculated from fugacity coefficients.
    sumy1=sumy1+y1(i);
end
for i=1:I
    if(i==1)
        if(abs(y(i)-y1(i))<1.0e-06)      % Check if old and new values for 'y' are within
            cond1=0;                      % tolerable limit for component 1.
        end
    end
    if(i==2)
        if(abs(y(i)-y1(i))<1.0e-06)      % Check if old and new values for 'y' are within
            cond2=0;                      % tolerable limit for component 2.
        end
    end
    y(i)=y1(i);                         %Change the value of 'y' to new.
end
end                                     % end of inner "while" loop
P1=P;
P=P*sumy1;                            %New guess value for pressure
end                                     % end of outer "while" loop
Ycal(j)=y(1);                          %Put calculated values of 'y' into vector.
Pthe(j)=P;                            %Put calculated values of pressure into vector.
end                                     % end of outer "for"loop
OF=0;OFP=0;OFP=0;
if((Ycal(1)==0)&(Yexpt(1)==0))
    OFY=0;
else
    OFY=OFY+(((Yexpt(1)-Ycal(1))/Yexpt(1))^2);
end
for i=2:n
    OFY=OFY+(((Yexpt(i)-Ycal(i))/Yexpt(i))^2); %Objective function of %composition.
end
for i=1:n
    OFP=OFP+(((Pexpt(i)-Pthe(i))/Pexpt(i))^2); %Objective function of pressure.
end
OF=OFY+OFP                                %Overall objective function.

```

% Code for function "qpi1.m" is given below.

```

function [phi]=qpi1(T,P,x,Tc,mu,vc,state,ki) %calculates fugacity coefficient.
R = 8.314/1000;
k0=1.2865;
k1=2.8225;
phi=[0,0];
for i=1:2
    mus(i)=(0.3976*mu(i)/(sqrt(R*Tc(i)*vc(i))));
    X2(i)=0.14988+0.97848*w(i)-0.01390*mus(i)+0.02928*mus(i)*mus(i);
    X3(i)=-0.32379+1.84591*w(i)+0.39338*mus(i)-0.25483*mus(i)*mus(i);
    X4(i)=0.14833-3.46693*w(i)-0.39170*mus(i)-0.01597*mus(i)*mus(i);
    X7(i)=-0.77357-1.45342*w(i)-0.04725*mus(i)-0.09669*mus(i)*mus(i);
    bei(i)=0.165*(vc(i))*((exp(-0.03125*(log(T/Tc(i))))-0.0054*((log(T/Tc(i)))^2))^3);
    ei(i)=(0.63189)*(1-0.81660*w(i)+3.25246*w(i)*w(i))*(vc(i));
    ai(i)=((1+X2(i)*(1-sqrt(T/Tc(i)))+X3(i)*((1-sqrt(T/Tc(i)))^2)+X4(i)*
        ((1-sqrt(T/Tc(i)))^3))^2)*(1.84713)*(1-0.05218*w(i)+1.06446*w(i)*w(i)
        -0.02730*mus(i)+0.02048*mus(i)*mus(i))*(R*vc(i)*Tc(i));
    ci(i)=((1+X7(i)*(1-sqrt(T/Tc(i))))^2)*(1.78336)*(1-1.29690*w(i)+2.78945*w(i)*w(i)
        +0.07000*mus(i)+0.01188*mus(i)*mus(i))*(R*vc(i)*Tc(i));
end
a=qamix(x,ai,ki); % EOS parameter 'a' for mixture
be=qbemix(x,bei); %EOS parameter 'beta' for mixture;
c=qcmix(x,ci,ki); %EOS parameter 'c' for mixture
e=qemix(x,ei); %EOS parameter 'e' for mixture
q3=(P/(R*T))*(-2*k0*be+e-(R*T/P)); % Coefficients of the
q2=((P/(R*T))^2)*(((R*T/P)*(be*(k0-k1)-e))+k0*be*(k0*be-2*e)+a/P); % quartic equation
q1=((P/(R*T))^3)*(e*(((k0*be)^2)+(R*T*be/P)*(k0-k1))+(k0*be*(c-a)/P)); % of compressibility
q0=((P/(R*T))^4)*(-c*((k0*be)^2)/P); % factor
ro=[1 q3 q2 q1 q0];
Z=roots(ro); % Roots (Compressibility factor) are found out.
Big=0;Small=0;
if(state==1)
    if((imag(Z(1))==0)&(real(Z(1))>=0))
        Big=real(Z(1));
    end
    if((imag(Z(2))==0)&(real(Z(2))>=0))
        if((real(Z(2)))>(real(Z(1))))
            Big=real(Z(2));
        end
    end
    if((imag(Z(3))==0)&(real(Z(3))>=0))
        if(Big<(real(Z(3))))
            Big=(real(Z(3)));
        end
    end
    if((imag(Z(4))==0)&(real(Z(4))>=0))
        if(Big<(real(Z(4))))
            Big=(real(Z(4)));
        end
    end
%Arrange the compressibility factors
%as vapor and liquid phase
% compressibility factors
end

```

```

end
end

Z1=Big;
end

if(state==0)
  if((imag(Z(1))==0)&(real(Z(1))>=0))
    Small=real(Z(1));
  end
  if((imag(Z(2))==0)&(real(Z(2))>=0))
    if((real(Z(2))<(real(Z(1))))) 
      Small=real(Z(2));
    end
  end
  if((imag(Z(3))==0)&(real(Z(3))>=0))
    if(Small>(real(Z(3)))) 
      Small=(real(Z(3)));
    end
  end
  if((imag(Z(4))==0)&(real(Z(4))>=0))
    if(Small>(real(Z(4)))) 
      Small=(real(Z(4)));
    elseif(Small==0)
      Small=real(Z(4));
    end
  end
  Z1=Small;
end

v1=Z1*R*T/P;
E1=(P*e/(R*T));
E2=((P*k0*be)/(R*T));
aij(1)=x(1)*ai(1)+x(2)*sqrt(ai(1)*ai(2))*(1-ki);
aij(2)=x(2)*ai(2)+x(1)*sqrt(ai(1)*ai(2))*(1-ki);
cij(1)=x(1)*ci(1)+x(2)*sqrt(ci(1)*ci(2))*(1-ki);
cij(2)=x(2)*ci(2)+x(1)*sqrt(ci(1)*ci(2))*(1-ki);

for i=1:2
  L1(i)=((k0*bei(i))/(v1-(k0*be)));
  L2(i)=((k1*bei(i)*v1)/((v1-(k0*be))^2));
  L3(i)=((k1*be)/(v1-(k0*be)));
  L4(i)=((1/(R*T))*(a/(k0*be+e))*((k0*bei(i)/(v1-(k0*be)))+(ei(i)/(v1+e))));
  L5(i)=((1/(R*T))*(c/(k0*be+e))*(((k0*bei(i)*ei(i))/(e*(v1+e)))-((k0*bei(i)/(v1-k0*be)))));
  L(i)=L1(i)+L2(i)+L3(i)+L4(i)+L5(i);

  M1(i)=(2*aij(i)/((k0*be)+e));
  M2(i)=-(a*(k0*bei(i)+ei(i))+c*(ei(i)-(k0*be*k0*bei(i)/e)))/((k0*be+e)^2));
  M3(i)=((k0*be*2*cij(i)+k0*bei(i)*c)/(k0*be*(k0*be+e)));

```

```

M4(i)=-(k0*bei(i)*c/(k0*be*e));
M(i)=M1(i)+M2(i)+M3(i)+M4(i);

N1(i)=-(2*aij(i))/((k0*be)+e));
N2(i)=((a*(k0*bei(i)+ei(i))+c*(ei(i)-(k0*be*k0*bei(i)/e)))/((k0*be+e)^2));
N3(i)=((k0*be*2*cij(i)+k0*bei(i)*c)/(e*(k0*be+e)));
N4(i)=-(ei(i)*c/(e*e));
N(i)=N1(i)+N2(i)+N3(i)+N4(i);

Q1(i)=-(k0*be*2*cij(i)+k0*bei(i)*c)/(k0*be*e));
Q2(i)=(c*(bei(i)*e+be*ei(i))/(be*e*e));
Q(i)=Q1(i)+Q2(i);
phi(i)=exp((L(i)+(1/(R*T))*(Q(i)*(log(Z1))+N(i)*(log(Z1+E1))+M(i)*(log(Z1-E2)))-(log(Z1-E2))));
end

```

```

% Code for calculating mixture parameters 'a','beta','c' and 'e'
"qamix.m","qbemix.m","qcmmix.m" and "qemix.m"
function a = qamix(x,ai,ki)
a=((x(1)^2)*ai(1)+(x(2)^2)*ai(2)+2.0*x(1)*x(2)*sqrt(ai(1)*ai(2))*(1.0-ki));

function be=qbemix(x,bei)
be=x(1)*bei(1)+x(2)*bei(2);

function c = qcmmix(x,ci,ki)
c=((x(1)^2)*ci(1)+(x(2)^2)*ci(2)+2.0*x(1)*x(2)*sqrt(ci(1)*ci(2))*(1.0-ki));

function e = qemix(x,ei)
e=x(1)*ei(1)+x(2)*ei(2);

```

A4 Program Code for VLE data by Model IV

% Matlab commands contained in the file “Modelq2.m”.

```

function Modelq2(); %Main function i.e. calls other functions to calculate optimum
%binary interaction parameters and VLE data corresponding to
kij=[0,0] %that values.
min=fmins('qsv',kij) %”min” is the vector containing the final interaction parameters
% where the objective function becomes minimum. ”qsv” is the
%function for VLE.”fmin” subfunction minimizing a function
%one variable using golden section search algorithm and the two
%values are the boundaries in which one tries to find the
% minima.

```

%Control is passed onto the file “qsv.m”. “qsv.m” contains the following commands.

Function OF=qpr(kij) %OF is the objective function value which is passed to the

%“fmin” function and “kij” is the value passed by “fmin”.

```
global I;
I=2; %Initialization of the required data.
j=1;STATEL=0;STATEV=1;
n=8; %Benzene&Heptane
Xexpt=[0.0000,0.3516,0.5252,0.5633,0.6083,0.6513,0.6731,1.0000]; % Vector with experimental 'x'
Yexpt=[0.0000,0.4748,0.6479,0.6671,0.7192,0.7351,0.7536,1.0000]; %Vector with experimental 'y'
Pexpt=[298.5,384.2,418.6,425.0,430.9,436.0,440.6,473.2]; %experimental 'P'
T=413.15; % temperature
Tc=[562.2,540.3]; %Critical temperature of components 1 and 2.
Pc=[48.9,27.4]; %Critical pressure of components 1 and 2.
vc=[0.259,0.432]; %Critical volumes of components 1 and 2.
mu=[0.0,0.0]; %Dipole moment of components 1 and 2
```

for j=1:n % Loop changing experimental ‘x’ values

```
x(1)=Xexpt(j);
x(2)=(1-x(1));
P=0;
psat(2)=Pexpt(1);
psat(1)=Pexpt(n);
P=x(1)*psat(1)+x(2)*psat(2); %Initial guess of total pressure
sumy1=0;
P1=0;
```

```
while(sumy1~=1)
    if(abs(P-P1)<1e-05)
        break;
    end
    for i=1:I
        k(i)=psat(i)/P;
        y(i)=k(i)*x(i); %Initial guess for vapor composition 'y'.
    end
    t=1;
```

```
[phi]= qpi1(T,P,x,Tc,Pc,mu,STATEL,kij); %Control passes to “qsvpi1.m” where fugacity
% coefficient for liquid phase is calculated. The code
% for “qsvpi1.m” is given at the bottom.
```

```
phil=phi;
cond1=1;cond2=1;
while(1)
    if((cond1==0)&(cond2==0))
        break;
    end
    t=1;
    [phi]=qpi1(T,P,y,Tc,Pc,mu,STATEV,kij); % Fugacity coefficient for the vapor phase is
% calculated using “qsvpi1.m”
phiv=phi;
sumy1=0;
for i=1:I
```

```

y1(i)=(phil(i)*x(i))/phiv(i); % y' is calculated from fugacity coefficients.
sumy1=sumy1+y1(i);
end
for i=1:I
    if(i==1)
        if(abs(y(i)-y1(i))<1.0e-06) % Check if old and new values for 'y' are within
            cond1=0; % tolerable limit for component 1.
        end
    end
    if(i==2)
        if(abs(y(i)-y1(i))<1.0e-06) % Check if old and new values for 'y' are within
            cond2=0; % tolerable limit for component 2.
        end
    end
    y(i)=y1(i); %Change the value of 'y' to new.
end
% end of inner "while" loop
P1=P;
P=P*sumy1; %New guess value for pressure
end % end of outer "while" loop
Ycal(j)=y(1); %Put calculated values of 'y' into vector.
Pthe(j)=P; %Put calculated values of pressure into vector.
end % end of outer "for"loop

OF=0;OFY=0;OFP=0;
if((Ycal(1)==0)&(Yexpt(1)==0))
    OFY=0;
else
    OFY=OFY+(((Yexpt(1)-Ycal(1))/Yexpt(1))^2);
end
for i=2:n
    OFY=OFY+(((Yexpt(i)-Ycal(i))/Yexpt(i))^2); %Objective function of %composition.
end
for i=1:n
    OFP=OFP+(((Pexpt(i)-Pthe(i))/Pexpt(i))^2); %Objective function of pressure.
end
OF=OFY+OFP %Overall objective function.

```

% Code for function "qsvpi1.m" is given below.

```

function [phi]=qpi1(T,P,x,Tc,mu,vc,state,ki) %calculates fugacity coefficient.
R = 8.314/1000;
k0=1.2865;
k1=2.8225;
phi=[0,0];
for i=1:2
    mus(i)=(0.3976*mu(i)/(sqrt(R*Tc(i)*vc(i))));
    X2(i)=0.14988+0.97848*w(i)-0.01390*mus(i)+0.02928*mus(i)*mus(i);

```

```

X3(i)=-0.32379+1.84591*w(i)+0.39338*mus(i)-0.25483*mus(i)*mus(i);
X4(i)=0.14833-3.46693*w(i)-0.39170*mus(i)-0.01597*mus(i)*mus(i);
X7(i)=-0.77357-1.45342*w(i)-0.04725*mus(i)-0.09669*mus(i)*mus(i);
bei(i)=0.165*(vc(i))*((exp(-0.03125*(log(T/Tc(i))))-0.0054*((log(T/Tc(i)))^2))^3));
ei(i)=(0.63189)*(1-0.81660*w(i)+3.25246*w(i)*w(i))*(vc(i));
ai(i)=((1+X2(i)*(1-sqrt(T/Tc(i)))+X3(i)*((1-sqrt(T/Tc(i)))^2)+X4(i)*
((1-sqrt(T/Tc(i)))^3))^2)*(1.84713)*(1-0.05218*w(i)+1.06446*w(i)*w(i)
-0.02730*mus(i)+0.02048*mus(i)*mus(i))*(R*vc(i)*Tc(i));
ci(i)=((1+X7(i)*(1-sqrt(T/Tc(i))))^2)*(1.78336)*(1-1.29690*w(i)+2.78945*w(i)*w(i)
+0.07000*mus(i)+0.01188*mus(i)*mus(i))*(R*vc(i)*Tc(i));
end
a=qamix(x,ai,ki); % EOS parameter 'a' for mixture
be=qbemix(x,bei); %EOS parameter 'beta' for mixture;
c=qcmix(x,ci,ki); %EOS parameter 'c' for mixture
e=qemix(x,ei); %EOS parameter 'e' for mixture
q3=(P/(R*T))*(-2*k0*be+e-(R*T/P)); % Coefficients of the
q2=((P/(R*T))^2)*(((R*T/P)*(be*(k0-k1)-e))+k0*be*(k0*be-2*e)+a/P); % quartic equation
q1=((P/(R*T))^3)*(e*((k0*be)^2)+(R*T*be/P)*(k0-k1))+(k0*be*(c-a)/P)); % of compressibility
q0=((P/(R*T))^4)*(-c*((k0*be)^2)/P); % factor
ro=[1 q3 q2 q1 q0];
Z=roots(ro) ; % Roots (Compressibility factor) are found out.
Big=0;Small=0;
if(state==1)
  if((imag(Z(1))==0)&(real(Z(1))>=0))
    Big=real(Z(1));
  end
  if((imag(Z(2))==0)&(real(Z(2))>=0))
    if((real(Z(2)))>(real(Z(1))))
      Big=real(Z(2));
    end
  end
  if((imag(Z(3))==0)&(real(Z(3))>=0))
    if(Big<(real(Z(3))))
      Big=(real(Z(3)));
    end
  end
  if((imag(Z(4))==0)&(real(Z(4))>=0))
    if(Big<(real(Z(4))))
      Big=(real(Z(4)));
    end
  end
  Z1=Big;
end

if(state==0)
  if((imag(Z(1))==0)&(real(Z(1))>=0))
    Small=real(Z(1));

```

```

if((imag(Z(2))==0)&(real(Z(2))>=0))
    if((real(Z(2)))<(real(Z(1))))
        Small=real(Z(2));
    end
end
if((imag(Z(3))==0)&(real(Z(3))>=0))
    if(Small>(real(Z(3))))
        Small=(real(Z(3)));
    end
end
if((imag(Z(4))==0)&(real(Z(4))>=0))
    if(Small>(real(Z(4))))
        Small=(real(Z(4)));
    elseif(Small==0)
        Small=real(Z(4));
    end
end
Z1=Small;
end

v1=Z1*R*T/P;
E1=(P*e/(R*T));
E2=((P*k0*be)/(R*T));

aij(1)=x(1)*ai(1)+x(2)*sqrt(ai(1)*ai(2))*(1-x(1)*ki(1)-
x(2)*ki(2))+x(1)*(x(2)^2)*sqrt(ai(1)*ai(2))*(ki(1)-ki(2));
aij(2)=x(2)*ai(2)+x(1)*sqrt(ai(1)*ai(2))*(1-x(1)*ki(1)-
x(2)*ki(2))+(x(1)^2)*x(2)*sqrt(ai(1)*ai(2))*(ki(2)-ki(1));
cij(1)=x(1)*ci(1)+x(2)*sqrt(ci(1)*ci(2))*(1-x(1)*ki(1)-
x(2)*ki(2))+x(1)*(x(2)^2)*sqrt(ci(1)*ci(2))*(ki(1)-ki(2));
cij(2)=x(2)*ci(2)+x(1)*sqrt(ci(1)*ci(2))*(1-x(1)*ki(1)-
x(2)*ki(2))+(x(1)^2)*x(2)*sqrt(ci(1)*ci(2))*(ki(2)-ki(1));

for i=1:2

L1(i)=((k0*bei(i))/(v1-(k0*be)));
L2(i)=((k1*bei(i)*v1)/((v1-(k0*be))^2));
L3(i)=((k1*be)/(v1-(k0*be)));
L4(i)=-(1/(R*T))*(a/(k0*be+e))*((k0*bei(i)/(v1-(k0*be)))+(ei(i)/(v1+e)));
L5(i)=((1/(R*T))*(c/(k0*be+e))*(((k0*bei(i)*ei(i))/(e*(v1+e)))-(k0*bei(i)/(v1-k0*be))));
L(i)=L1(i)+L2(i)+L3(i)+L4(i)+L5(i);

M1(i)=(2*aij(i)/((k0*be)+e));
M2(i)=-(a*(k0*bei(i)+ei(i))+c*(ei(i)-(k0*be*k0*bei(i)/e)))/((k0*be+e)^2);
M3(i)=((k0*be^2*cij(i)+k0*bei(i)*c)/(k0*be*(k0*be+e)));
M4(i)=-(k0*bei(i)*c/(k0*be*e));
M(i)=M1(i)+M2(i)+M3(i)+M4(i);

```

```

N1(i)=-(2*aij(i))/((k0*be)+e));
N2(i)=((a*(k0*bei(i)+ei(i))+c*(ei(i)-(k0*be*k0*bei(i)/e)))/((k0*be+e)^2));
N3(i)=((k0*be*2*cij(i)+k0*bei(i)*c)/(e*(k0*be+e)));
N4(i)=-(ei(i)*c/(e*e));
N(i)=N1(i)+N2(i)+N3(i)+N4(i);

Q1(i)=-(k0*be*2*cij(i)+k0*bei(i)*c)/(k0*be*e);
Q2(i)=(c*(bei(i)*e+be*ei(i))/(be*e*e));
Q(i)=Q1(i)+Q2(i);

phi(i)=exp((L(i)+(1/(R*T))*(Q(i)*(log(Z1))+N(i)*(log(Z1+E1))+M(i)*(log(Z1-E2)))-(log(Z1-E2))));

end

```

% Code for calculating mixture parameters ‘a’,‘beta’,‘c’ and ‘e’
“qsvamix.m”,“qsvbemix.m”,“qsvcmix.m” and “qsvemix.m”

```

function a = qsvamix(x,ai,ki)
a =((x(1)^2)*ai(1)+(x(2)^2)*ai(2)+2.0*x(1)*x(2)*sqrt(ai(1)*ai(2))*(1.0-x(1)*ki(1)-x(2)*ki(2)));

function be=qsvbemix(x,bei)
be=x(1)*bei(1)+x(2)*bei(2);

function c = qsvcmix(x,ci,ki)
c =((x(1)^2)*ci(1)+(x(2)^2)*ci(2)+2.0*x(1)*x(2)*sqrt(ci(1)*ci(2))*(1.0-x(1)*ki(1)-x(2)*ki(2)));

function e = qsvemix(x,ei)
e=x(1)*ei(1)+x(2)*ei(2);

```